THE PYROLYSIS OF VINYL BENZOATE

by

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SUMMARY.

This work describes a study which has been made of some of the physical aspects of the vapour-phase pyrolysis of the high-boiling ester, vinyl benzoate, the project being part of a wider study of the pyrolysis of "Terylene" which has been pursued in these laboratories.

The major part of the work involves a technique which is described whereby the rate of degradation of the involatile ester is followed empirically by measuring the rate of gas evolution from a system containing the vapourised ester together with a quantity of liquid reflux. Analysis of the pyrolysate gases is also applied to track the reaction.

The primary findings of the study are the following: the complex degradation reaction is found to be mainly homogeneous; evidence for the absence of free-radical chain reactions is presented, and three individual primary decomposition routes are concluded to proceed by molecular mechanisms; catalytic effects in the presence of carbonaceous

deposits, benzoic acid, and iodine are recorded.

A short parallel study of the pyrolysis of vinyl acetate is also reported. The reaction is concluded to be homogeneous, and involving no free-radical chain processes.

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1. INTRODUCTION.

The thermal stability of organic compounds has been the subject of an increasingly complex field of research for many years, and the qualitative nature of the degradation of many substances is now well established.[1]

In recent years, with the onset of a large synthetic polymer industry, it has become important to investigate the behaviour of many of these materials at elevated temperatures. In these laboratories attention has been focused on the degradation of polyester systems, and, in particular, a systematic study has been made of the commercially important polyester, poly(ethylene terephthalate), marketed in this country as "Terylene".

Early studies[2] indicated that an investigation of the pyrolysis of "Terylene" itself would prove a difficult task, because of the uncertainties involved in the interpretation of complex results. Thus it was decided that a more fruitful examination could be made by investigating the behaviour of model compounds, i.e., of relatively simple esters and related compounds which could be regarded as representing segments of the polymer chain, or products of the degradation of such segments.

Hence these investigations have been concerned in the main with simple esters, rather than polyesters. The breakdown of such esters has in itself led to a diversity of results; a brief summary, therefore, of the routes of ester pyrolysis is made below. The nomenclature used to denote the various modes of breakdown is that which has been developed in these laboratories in recent years.

1.1. The Pyrolysis of Esters.

The classical route for the thermal decomposition of an ester may be represented by the equation:-

$$R.CO.O.CH_2.CH_2.R' \longrightarrow R.CO.OH + CH_2=CHR'$$

i.e. ester $\longrightarrow$ acid + olefin

However, the many examples of ester pyrolysis which are now available clearly indicate that the above scission is only one of several readily identified routes, and that, while the above equation represents a route of primary importance, it need not be the major route in any particular case.

Thus, although examples are known of esters decomposing smoothly by one route only,[3,4] the general case presents a number of primary breakdown routes. For example, allyl acetate decomposes by two primary routes,[5] phenyl acrylate by four primary routes,[6] iso-propenyl acetate by five primary routes.[7] In

addition, decomposition of the resulting compounds can often occur, leading to a number of secondary and tertiary routes.

Several factors will contribute towards the nature of any one pyrolysis. The number of resulting routes, and the extent to which each takes place, will be dependant upon the number of points of scission available, i.e., upon the complexity of the molecule; the physical characteristics of the molecule, such as the polarity of the groupings, and steric effects; and the number of labile hydrogen atoms available to take part in any changes. Such factors will be inter-dependant. Temperature will also affect the reaction, higher temperatures giving rise to new routes, primary or otherwise. The individual types of ester decomposition will now be considered.

1.1.1. Alkyl-oxygen scission - Route A.

This type of scission, the most important single route in ester pyrolysis, involves a breaking of the ether oxygen of the ester group from the attached hydrocarbon group, and may be subdivided into two types, depending upon the unsaturation or otherwise of the α- and β-carbon atoms:-

$$R.CO.O.CH_2.CH_2.R' \longrightarrow R.CO.OH + CH_2{=}CHR' \quad - - A^1$$

$$R.CO.O.CH{=}CHR' \longrightarrow R.CO.OH + CH{\equiv}CR' \quad - - - A^2$$

The change necessitates the presence of a β-hydrogen atom, which is transferred in the process. Hence ethyl acetate[8] decomposes according to the equation:-

$$CH_3.CO.O.CH_2.CH_3 \longrightarrow CH_3.CO_2H + CH_2{=}CH_2 \quad - - A^1$$

A corresponding A^2 decomposition is afforded by the pyrolysis of vinyl acetate,[9,10] although this is a very minor route in the total breakdown:-

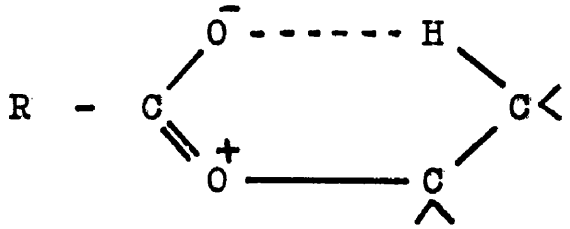
$$CH_3.CO.O.CH{=}CH_2 \longrightarrow CH_3.CO_2H + CH{\equiv}CH \quad - - - A^2$$

The readiness with which an alkyl-oxygen scission may take place has been clearly demonstrated by Hurd and Blunk's[11] studies of the pyrolysis of n-, sec-, and tert-alkyl carboxylates. They found that while tert-butyl acetate pyrolysed at 300°C to give the acid and olefin only, iso-propyl acetate required a temperature of 430°C, and ethyl acetate a temperature of 525°C, to give corresponding degrees of breakdown, and the latter two cases were accompanied, moreover, by secondary decomposition.

Similarly, McColl,[12] in a survey of published results, has shown that, at 400°C, the relative rates of decomposition to acid and olefin for ethyl, iso-propyl, and tert-butyl acetates, are in the ratios 1 : 26 : 515. The corresponding formates show the same trend, while indicating at the same time that a

change in the acid group of an ester has relatively little effect on the stability of the compound. Thus the rate ratio for ethyl acetate to ethyl formate is 0.97, for tert-butyl propionate to tert-butyl acetate, 0.79.

While such observations clearly infer that the susceptibility of an ester to undergo alkyl-oxygen scission is associated with the number of labile β-hydrogen atoms which are available to take part in the reaction, this factor is not in itself sufficient to explain the magnitude of the rate changes on moving from a primary to a tertiary ester. McColl[12] has shown in his discussion that these ester elimination reactions bear a strong analogy to E.2. eliminations, and has suggested that, in the transient six-membered ring suggested by Hurd and Blunk (referred to later in this work), the forming O-H bond principally determines the rate. The transition state may be set down as follows :-



and such a structure will be stablilised by the inductive α-methyl substitution, thus explaining the observed rate sequence.

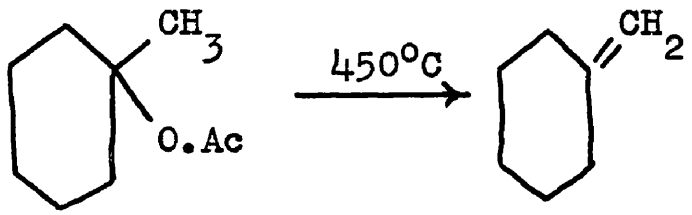
In the case of an unsymmetrical branched chain

ester, two different olefins can arise by an A^1 scission. For example, Houtman, van Steenis, and Heertjes[13] found that, on pyrolysis, sec-butyl acetate yielded two olefinic products :-

$$CH_3.CH_2.CH(Me).OAc \xrightarrow{500^oC} \underset{56\%}{CH_3.CH_2.CH=CH_2} + \underset{44\%}{CH_3.CH=CH.CH_3}$$

Two rules may be applied to elimination reactions. The Hofmann rule,[14] in its most general form, states that elimination from a quaternary ammonium hydroxide will lead to preferential formation of that olefin carrying the smallest number of attached alkyl groups; the Saytzeff rule,[14] applied to secondary and tertiary alkyl bromides, states that elimination will lead to preferential formation of that olefin carrying the largest number of attached alkyl groups. In the above example of acid elimination from an ester, and in other like cases, both rules are obviously in operation.

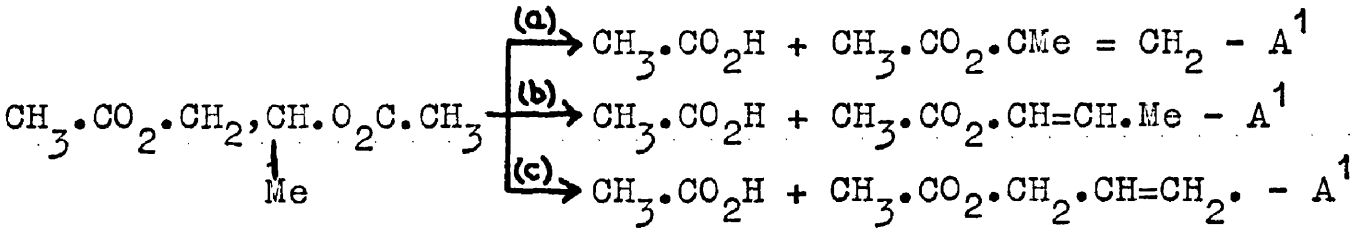
However, Bailey and co-workers,[15,16,17,18,19] by pyrolysing secondary and tertiary esters under conditions such that no carbonisation took place, were able to produce one olefin only by alkyl-oxygen scission. Thus 1-methylcyclohexylacetate gave exclusively methylenecyclohexane :-



+ Ac.OH - - A^1

In the light of these studies, Bailey and King concluded[19] that gas phase eliminations from esters may be regarded, in general, as being governed by the Hofmann rule.

Their conclusions are in agreement with the interesting result given by propylene diacetate,[5] which contains three differently substituted β-hydrogen atoms, and could therefore formally undergo three competitive A^1 scissions :-



In fact, careful investigations revealed that only route (c) was followed.

Recent workers, however, carrying out investigations independently of each other, have examined a number of aliphatic and alicyclic acetates[20,21,22.] and have claimed that, even under carefully controlled conditions of pyrolysis, the elimination is random, resulting in a mixture of isomers. In a re-examination of previous work, Bailey and Hale[23] have failed to reproduce previous results pointing to selectivity of elimination, and have agreed that the conditions required to produce one isomer exclusively are 'highly elusive'. In view of these, and other,

conflicting results, no conclusions can be confidently drawn at present.

1.1.2. Acyl-oxygen scission - Route B.

In contrast to alkyl-oxygen scission, acyl-oxygen scission involves transfer of a hydrogen atom α- to the ester grouping. The hydrogen atom can migrate from one of two sites, each case leading to different products; a sub-division of this type of breakdown, therefore, can again be made :-

$$R.CH_2.CO.O.CH_2.R' \begin{cases} \rightarrow R.CH{=}CO + R'.CH_2.OH & - - - \ B^1 \\ \rightarrow R.CH_2.CHO + R'.CHO & - - - \ B^2 \end{cases}$$

This is normally a very minor route in ester pyrolysis, but it can become of major importance in the case of esters lacking a β- hydrogen atom. A good example is afforded by phenyl acetate which decomposes exclusively by a B^1 scission[11] :-

$$CH_3.CO.O.Ph \xrightarrow{625^0C} CH_2{=}CO + Ph.OH \quad - - - \ B^1$$

By a B^2 scission, methyl acetate gives two aldehydic fractions, amongst other products[24] :-

$$CH_3.CO.O.CH_3 \xrightarrow{1100^0C} [CH_3.CHO + H.CHO] \quad - - \ B^2$$

$$\downarrow$$

Secondary products.

In general, an ester must be subjected to relatively high temperature, before acyl-oxygen scission can be induced.

1.1.3. Decarbonylation - Route C^1

Decarbonylation, that is, the loss of carbon monoxide, is a reaction characteristic of aldehydes and ketones rather than esters. Therefore, when decarbonylation occurs in ester pyrolysis, it normally does so in esters containing an aldehydic or ketonic carbonyl grouping. Calvin and Lemman,[25] by using carbon monoxide isotope techniques, have demonstrated the elimation of carbon monoxide from the ester grouping in ethyl pyruvate.

Recently, Allan, Forman, and Ritchie[10] have shown that, in the case of vinyl esters, what appears to be a decarbonylation of the ester is, in fact, a re-arrangement of the ester to the corresponding β-ketoaldehyde, which then loses carbon monoxide as would be expected. The reaction for vinyl benzoate may be formulated thus :-

$$Ph.CO.O.CH{=}CH_2 \longrightarrow [Ph.CO.CH_2.CHO] \quad - - - - \quad R$$

$$\longrightarrow Ph.CO.CH_3 + CO \quad - - - - \quad C^1$$

Phenyl formate provides an example[26] of an ester with no associated ketonic carbonyl group undergoing de-carbonylation, and the formation of phenol and carbon monoxide from phenyl acrylate and phenyl methacrylate[6] has been shown to be <u>via</u> the formation of phenyl formate.

$$CH_2{=}CH.CO_2.Ph \longrightarrow [H.CO_2Ph] + CH{\equiv}CH \quad - - \quad A^2$$
$$\downarrow$$
$$Ph.OH + CO \quad - - - - \quad C^1$$

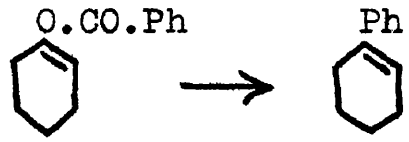
1.1.4. Decarboxylation - Route C^2

While decarboxylation of carboxylic acids is a well established reaction,[1] ester decarboxylation was once thought to be a very unusual mode of thermal decomposition. Until recently, the examples quoted in literature were few. One well known case of ester decarboxylation is given by the pyrolysis of phenyl maleate (or fumarate)[27,28] :-

$$Ph.O_2C.CH{=}CH.CO_2Ph \longrightarrow PhCH{=}CH.Ph + CO_2 \quad - A^2$$

Anschütz[29] has further demonstrated this reaction to be general for aryl esters of cinnamic acid.

Much more recently, it has been shown[7,10] that the decomposition pattern for enol carboxylates in general (including vinyl esters) embraces decarboxylation as a minor, but nevertheless significant, primary breakdown route. Thus, on pyrolysing cyclohex-1-enyl benzoate[7] at 500°C, decarboxylation occurred to the extent of about 10% of the total breakdown :-



$$+ \quad CO_2 \quad - - - - \quad C^2$$

Yet another recently discovered example[6] is the decarboxylation of phenyl acrylate (along with the

α-methacrylate) :-

$$CH_2{=}CH.CO_2Ph \xrightarrow[13\%]{550^oC} CH_2{=}CH.Ph + CO_2 - - -C^2$$

A notable feature of all the above quoted examples of ester decarboxylation, and one which is evident in other known examples, is that the esters undergoing this reaction are saturated. This, indeed, appears to be the general case, certainly where decarboxylation occurs to any noticeable extent. However, Bennet, Jones, and Ritchie[30] have noted that α:α'-dicyanobenzyl benzoate, a fully saturated ester, undergoes decarboxylation; but the reaction may be influenced by the unsaturated C≡N grouping.

$$Ph.CO_2CPh(CN)_2 \longrightarrow CPh_2(CN)_2 + CO_2 - - C^2$$

1.1.5. Disproportionation - Route D

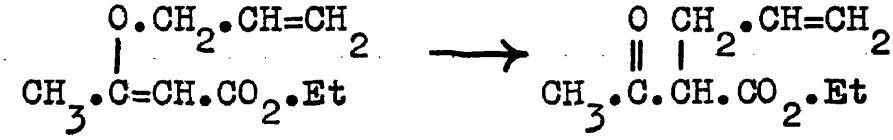
This type of scission involves the breaking of an ester, usually unsymmetrical, into two fragments, which in general may be expected to be more symmetrical than the original compound. Cretcher and Pittenger[31] have demonstrated this phenomonen by an examination of the half-esters of ethylene glycol. The reaction may be represented by the general equation :-

$$2\ Ar.CO_2.CH_2.CH_2.OH \longrightarrow Ar.CO_2.CH_2.CH_2.O_2C.Ar - D + HO.CH_2.CH_2.OH$$

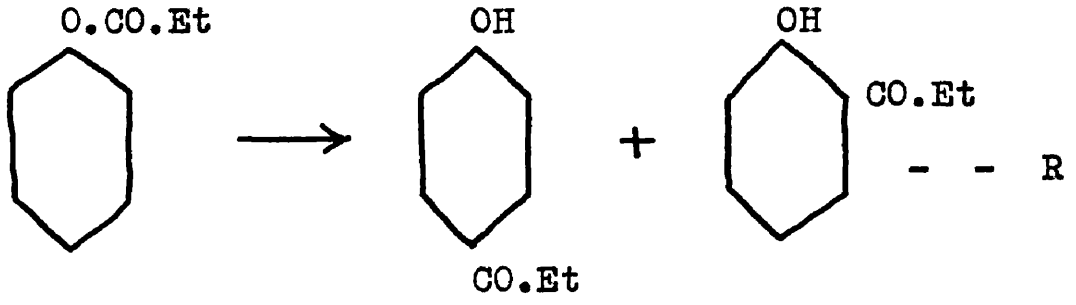
1.1.6. Re-arrangement - Route R

Ester re-arrangement reactions are varied in

character, and cannot therefore be brought into a general classification scheme to the same degree as the variety of reactions illustrated above. Such reactions may or may not involve specific catalysts; moreover, they may or may not involve a scission, or shift, of the ester group itself. Thus the conversion of ethyl O-allylacetoacetate to ethyl α-allylacetoacetate,[33] which is really an example of the Claisen re-arrangement (occurring with allyl ethers of phenol or enols), can be brought about thermally :-



while the Fries re-arrangement of phenyl propionate requires the presence of a Friedel-Crafts catalyst such as aluminium chloride, and involves a scission of the ester group :-



Of particular interest to this present work is the now well established thermal re-arrangement of many enol carboxylates to their isomeric β-diketones. The general reaction may be represented as follows :-

$$R.CO_2.CR'=CHR'' \longrightarrow R.CO.CHR''.CO.R' \quad - - - \quad R$$

Wislicenus[34] reported the first known example of this thermal reaction as early as 1905, although the following reaction was recognised as a base-catalysed conversion[35] :-

$$Me.CO.O.CMe=CH.CO_2Et \longrightarrow Me.CO.CH(CO_2Et).CO.Me \quad - R$$

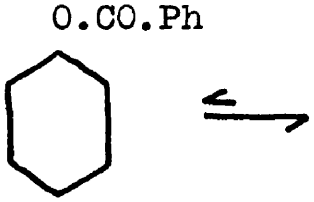
The general nature of the reaction, however, was not appreciated until Young and co-workers[36,37] studied a number of such carboxylates. They demonstrated, for example, that the enol benzoate of acetone can be converted to benzoylacetone as follows :-

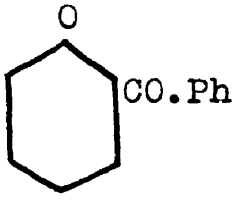
$$CH_3C(O.CO.Ph)=CH_2 \xrightarrow{500^oC} Ph.CO.CH_2.CO.CH_3 \quad - - \quad R$$

Allan, McGee, and Ritchie[7] have since shown the unexpected fact that the re-arrangement is a reversible reaction, with the equilibrium lying well over to the β-diketone stage; hence the pyrolysis of acetoylacetone at 500°C was found to yield small quantities of isopropenyl acetate :-

$$Me.CO.CH_2.CO.Me \rightleftharpoons AcO.CMe.=CH_2 \quad - - - \quad R$$

Another interesting example quoted by these workers is that of the cyclic enol, cyclohex-1-enyl benzoate, which is converted to 2-benzoylcyclohexanone :-





$$- - - - - - - \quad R$$

In particular, this arrangement has been applied successfully to the special case of vinyl esters[10] in order to account for otherwise unexpected products of the thermal decomposition of these esters. The vinyl esters will be considered in the next section of this work, along with certain proposed mechanisms of the reaction.

It has also been shown that the enol carboxylate re-arrangement can be induced catalytically by the use of boron triflouride at low temperatures, the suggested intermediate being a complex addition compound.[37]

1.2. The Pyrolysis of "Terylene" and Related Esters.

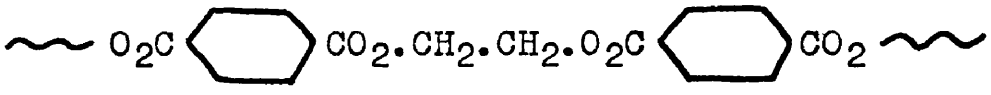
The pyrolysis of the polymer poly(ethylene terephthalate), or "Terylene", has been the subject of a number of investigations. Pohl[38] attacked the problem by measuring the rate of gas evolution at temperatures of about 300°C, and concluded that random main-chain scission was occurring. He was also able to detect acetaldehyde, water, and carbon dioxide in the pyrolysate, and, in addition, carboxyl and anhydride groups. He suggested that the methylene group β- to the ester group was a major point of weakness.

A kinetical study by Marshall and Todd,[39] in which they examined changes in the melt viscosity of the

polymer, again at temperatures of round about 300°C, indicated, as Pohl's studies had done, that random main-chain scission was taking place, probably at the ester linkage, producing one carboxyl group per scission. Acetaldehyde and carbon dioxide were again detected, along with carbon monoxide, terephthalic acid, and an unidentified solid thought to be a mono-alkyl ester of terephthalic acid, or an acid dimer. A free-radical degradation sequence was tentatively outlined.

Initial studies[2] in these laboratories revealed the presence of high-boiling carbonyl compounds in the degraded ester. At this stage, it was evident that pyrolysis of the polymer would lead to a complexity of results, and so attention was turned to model compounds. This work has revealed a much more complete understanding of the qualitative nature of the degradation of "Terylene", and much of the work has now been published.[10,40,41]

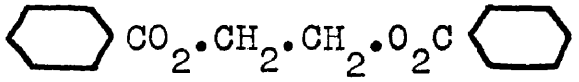
A brief consideration of a segment of the "Terylene" chain immediately suggested a number of primary model compounds :-



poly(ethylene terephthalate)

The chosen models typified the polyester shown above, or contained end-groupings or ether linkages which are known to occur in the polycondensate.

In particular, one of the first model compounds selected was ethylene dibenzoate :-

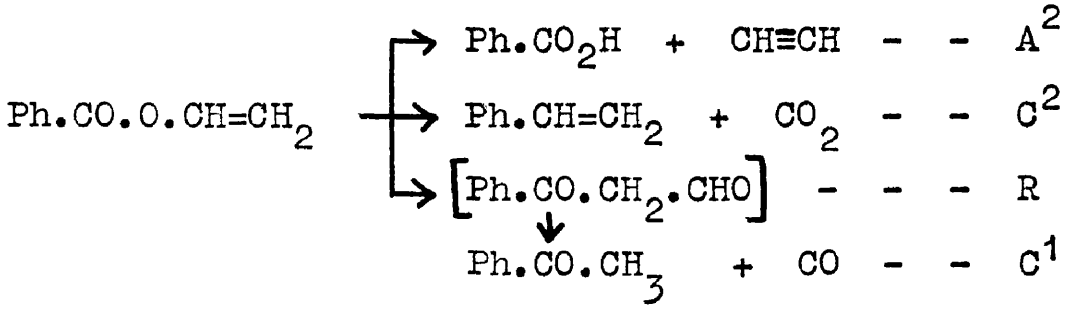


The pyrolysis of ethylene dibenzoate had been reported previously; Chitwood[42] found that, at 360-425°C, the ester yielded vinyl benzoate and benzoic acid, in accordance with the normal alkyl-oxygen scission.

Thus vinyl benzoate, the ester upon which this present work is based, was included in the scheme of model compounds.

1.2.1. The pyrolysis of vinyl benzoate.

The work of Allan, Forman, and Ritchie[10] has revealed that vinyl benzoate pyrolyses by three competitive primary routes in the temperature range 350-550°C. These routes may be formulated in the following scheme :-

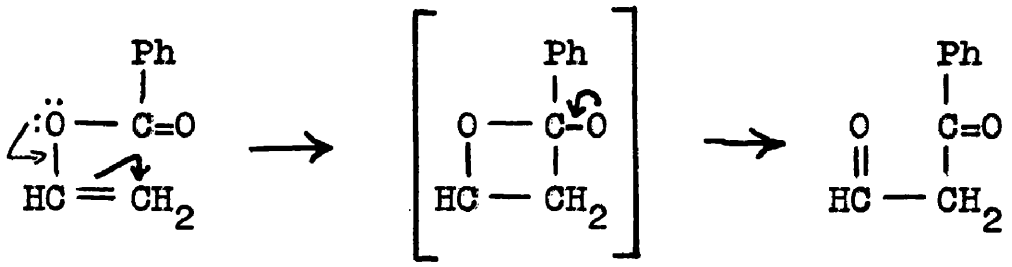


Based on the resultant gas analysis, route R/C^1, the major route, accounts for approximately 70-80% of the total breakdown, route C^2 for 10-20% of the total, and route A^2 for 5-10% of the total.

Primary routes in the pyrolysis of vinyl benzoate.

Route R/C^1 is of chief interest and importance. The intermediate arising from a re-arrangement of vinyl benzoate, benzoylacetaldehyde, was first suggested by the analogous re-arrangements of enol carboxylates,[36,37] already referred to in Section 1.1.6. Although, subsequently, a careful search failed to reveal the presence of any of the β-ketoaldehyde in the pyrolysate from vinyl benzoate, it was shown that the compound itself, on pyrolysis, gave, almost exclusively, carbon monoxide and acetophenone. The considerable instability of benzoylacetaldehyde had already been known.[43]

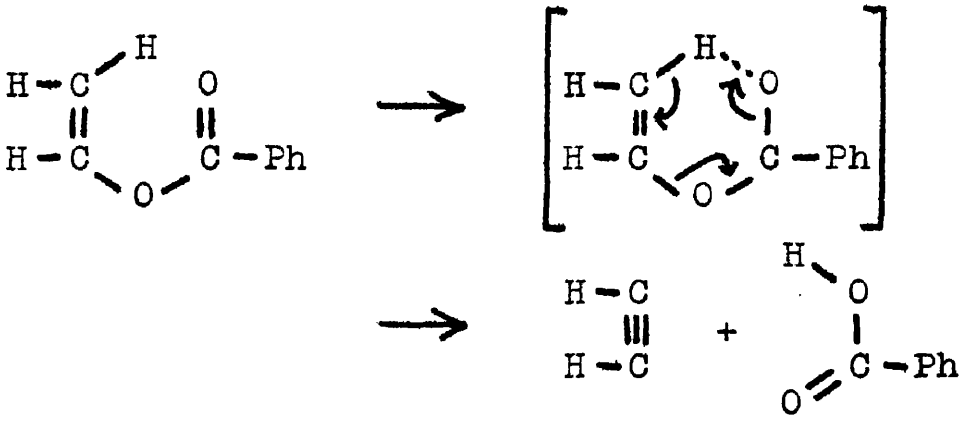
Young[37] has suggested a possible intramolecular mechanism for the thermal re-arrangement of enol carboxylates, involving a cyclic transition state, which may be conveniently applied to vinyl benzoate as follows :-



This re-arrangement is then followed by decarbonylation of the resultant β-keto-aldehyde.

The decarboxylation reaction, route C^2, adds yet another example to the comparitively small number of known ester decarboxylations. No mechanism has yet been postulated for this reaction, which involves the breaking of two bonds. As in other cases, it is noticeable that the ester concerned contains an unsaturated group, and it seems likely that this, in fact, is a controlling condition in the ability that an ester may have to undergo decarboxylation.

The smallest of the three primary routes, route A^2, may be compared to alkyl-oxygen scission of saturated esters. Hurd and Blunk[11] have postulated a molecular mechanism involving a six-membered chelate ring for saturated esters which might be applied to vinyl benzoate in the following manner :-



While a four-membered ring intermediate has been suggested[12] to account for the mechanism of these

A-type elimination reactions, the scheme outlined above is to be preferred because of the lesser degree of strain involved in the six-membered ring.

Secondary routes in the pyrolysis of vinyl benzoate.

A number of products which could not be accounted for by any primary degradation of vinyl benzoate were detected in the pyrolysate in small amounts, viz., benzene, methane, ethylene, and an unassigned band at 1140 $cm.^{-1}$ which appeared consistently in the infra-red spectrum of the gaseous pyrolysate.

Benzene will arise from the decarboxylation of benzoic acid. Methane is a decomposition product of acetaldehyde, which would arise in small quantity as an impurity in vinyl benzoate, or by interaction between the ester and the benzoic acid produced to give ethylidene dibenzoate, which in turn decomposes to benzoic anhydride and acetaldehyde [5] :-

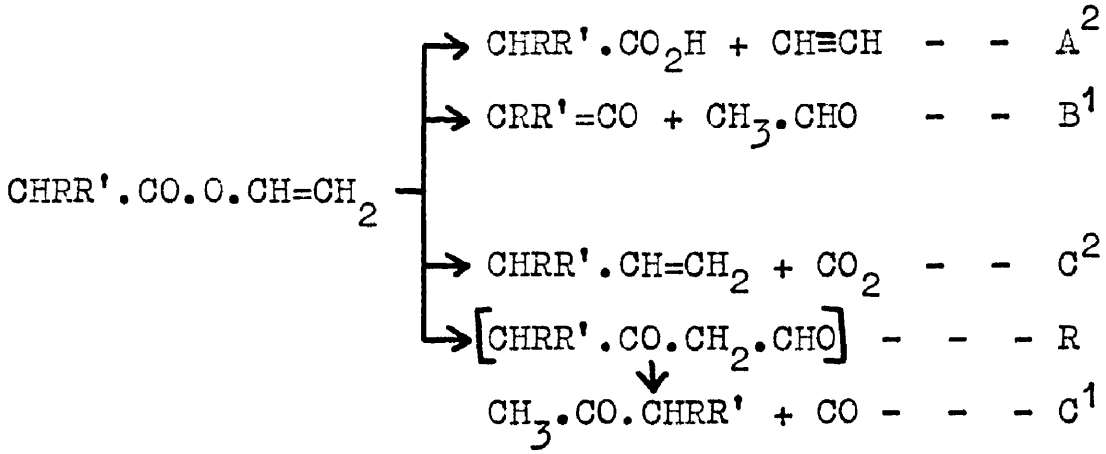
$$Ph.CO.O.CH=CH_2 + Ph.CO_2H \longrightarrow (Ph.CO.O)_2.CH.CH_3$$
$$\downarrow$$
$$(Ph.CO)_2.O + CH_3.CHO - D$$

The production of ethylene, and the unassigned infra-red band, could not be accounted for.

1.2.2. The pyrolysis of vinyl acetate and vinyl iso-butyrate.

Parallel studies on the pyrolysis of the vinyl esters of acetic acid and iso-butyric acid have

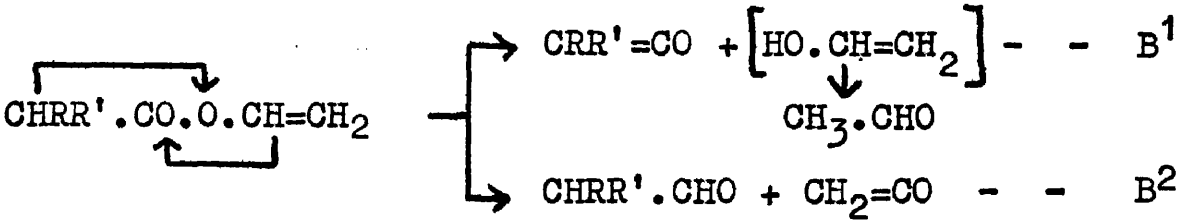
indicated[10] that, in addition to the three routes shown by vinyl benzoate, the aliphatic esters degrade by a fourth primary route. The general reaction scheme may be represented as follows :-



These esters are rather more stable than the corresponding benzoate, and pyrolyses were carried out in the range 500-550°C.

The gas analyses indicate that, for the acetate, routes B^1 and R/C^1 are of equal importance, each accounting for over 45% of the total breakdown, while routes A^2 and C^2 are very minor. For the iso-butyrate, route R/C^1 is the major route (over 60% of total breakdown), route B^1 accounts for a further 30% of the products, while the two remaining routes are very minor again.

Route B^1 only need be discussed, as the same comments as were made for vinyl benzoate may be applied to the other three routes. There are two hydrogen transfers which could lead to acyl-oxygen scission of these esters, viz :-



In the case of the acetate, either a B^1 or a B^2 scission leads to the same products, but for vinyl iso-butyrate the two routes are distinguishable, and, in fact, a B^1 scission only was found to be taking place. Moreover, while for vinyl benzoate a B^1 scission is not formally possible because of its structure, a B^2 scission is possible, but no evidence for this was detected. Thus it is clear that vinyl esters undergo acyl-oxygen scission by a B^1 route only.

No general mechanism has been formulated for acyl-oxygen scission, although a free-radical breakdown has been suggested in the particular case of methyl phenylacetate[11]. Certainly the high temperature required to induce acyl-oxygen scission in many cases suggest that radical processes may be playing a major part in this mode of decomposition.

1.3. Physico-chemical Studies on Thermal Decompositions in the Gas Phase.

Decomposition reactions of organic substances in the gas phase have been the subject of many studies over a large number of years, and much information is now

available with regard to the kinetics and mechanisms of a wide variety of systems.[44,45.]

While the characteristics of such reactions are too diverse to summarise briefly, the experimental techniques[46] which have been applied to these many gas-phase systems are essentially the same, and may be divided broadly into two classes.

The first, and most widely used, method is the static method, whereby a known concentration of the compound under examination is introduced, in the vapour phase, into a heated, evacuated, vessel, and the pressure changes in the system followed on a manometer or pressure gauge incorporated into the unit. From the pressure-time plots so obtained, under varying reaction conditions, the kinetics and mechanisms of the reaction can be deduced, the pressure changes being equated to the changes in concentration of the reactants and products in the system. The static method is an indirect means of following the course of a reaction, and it is desirable, where possible, to supplement this information by direct chemical analysis of the reaction mixtures.

The second general technique applied to gas-phase systems is the flow method, whereby the reactant is passed, in the gas-phase, through a

heated chamber, the products collected, and analysed. By correlating the volume of the reaction chamber, the concentration and flow rate of the reactant, and the analysis of the products, the required kinetical and mechanistic information can be obtained. A carrier gas may be used to transport the reactant, and if a gas such as toluene, a noted free-radical inhibitor, is employed, this is likely to lead to suppression of free-radical processes which may normally play a major part in the decomposition.

1.3.1. Kinetic studies of ester pyrolysis.

Applying the general principles described above, a number of investigations have been made of the thermal decomposition of some esters, mainly formates and acetates.

Thus, for example, Makens and Eversole[47] studied the decomposition of ethyl formate into formic acid and ethylene, using a static method and found the reaction to be homogeneous, (i.e. a true gas-phase reaction, as distinct from a heterogeneous reaction, where a reaction which is apparently in the gas-phase actually takes place at the walls of the reaction vessel), of first order, and having an activation energy of 40 k.cal./mole. A later investigation[48] of ethyl formate, amongst other esters, by Blades,

in which he employed the flow technique using toluene as a carrier gas, gave an activation energy for the inhibited reaction of 44 k.cal./mole. Similar studies of the pyrolysis of n-propyl formate,[49] tert-butyl acetate,[50] tert-butyl propionate,[51] (-)-menthyl benzoate,[3] and tert-butyl formate[52] have indicated that all of these decompositions are homogeneous reactions of the first order, with activation energies ranging from 35-45 k.cal./mole. In all of these cases, experimental conditions were such that the reaction studied was the alkyl-oxygen scission to acid and olefin, other primary routes and secondary decompositions being small enough to ignore. No intensive search has been made for free-radical reactions in these decompositions, although Gordon, Price, and Trotman-Dickenson[52] report that cyclohexene, a free-radical inhibitor, had no effect on the decomposition of tert-butyl formate. A limited number of investigations have been made of esters decomposing by routes other than an alkyl-oxygen scission. Thus Steacie[53] found that methyl formate decomposed heterogeneously according to the equations :-

$$H.CO_2.CH_3 \xrightarrow{\text{fast}} CH_3.OH + CO \quad - - - - \quad c^1$$

(principal reaction).

$$CH_3.OH \xrightarrow{\text{slow}} H.CHO + H_2$$

$$\downarrow$$

$$CO + H_2$$

He attributed an activation energy of 48.7 k.cal./mole to the overall reaction.

Coffin[54] investigated the disproportionation of ethylidene diacetate to acetic anhydride and acetaldehyde, and concluded that the decomposition was homogeneous, and of the first order.

1.3.2. Mechanisms in ester pyrolysis.

Apart from Hurd and Blunk's[11] suggested six-membered chelate ring formation to account for A-type scissions, no general mechanisms have been formulated for ester pyrolyses reactions. This subject will be discussed in fuller detail in Section 5 of this work.

2. OBJECT OF THIS WORK.

With due regard to the work described in Section 1 of this thesis, it was decided that a study of some of the physico-chemical processes involved in ester pyrolysis should be undertaken.

The ester chosen for this main study was vinyl benzoate. This choice was governed by two factors; (a) firstly, the ester was related to the wider study of the pyrolysis of "Terylene" which had been undertaken in these laboratories, (b) the ester was known to decompose by three routes only, one of these routes (R/C^1), moreover, dominating the reaction. It was thought that such a system would lend itself to simpler interpretation of results.

In the course of the work, it was hoped :-

(i) to study the kinetics of the gas-phase pyrolysis of vinyl benzoate.

(ii) to investigate the mechanisms involved in the degradation reactions.

3. EXPERIMENTAL.

3.1. Preparation of Compounds.

3.1.1. Vinyl benzoate.

Two routes were used to prepare vinyl benzoate samples for pyrolysis :-

(a) By the pyrolysis of ethylene dibenzoate.[42]

One mole of ethylene glycol was dissolved in pyridine, and treated with two moles of benzoyl chloride. The reaction mixture was poured into ice-cold water, and the crystals of ethylene dibenzoate filtered off and recrystallised from ethanol. M.pt. of crystals, 71-73°C.(73°C).

100 gm. of ethylene dibenzoate were pyrolysed under nitrogen in the liquid phase in a round-bottomed flask, the still-head temperature being adjusted to 235-240°C. The distilled fraction was taken up in ether, undissolved benzoic acid filtered off, the solution washed with 10% sodium carbonate solution, and dried. The vinyl benzoate was obtained by distillation, and purified by redistillation. B.pt. of fraction collected, 107°C/30 mm.

(b) By the ester-interchange reaction.[55]

One mole of benzoic acid was dissolved in three-and-a-half moles of vinyl acetate, and 3.5 gm.

mercuric acetate and 0.5 gm. concentrated sulphuric acid added. The whole was refluxed at 80°C for three hours, cooled, and anhydrous sodium acetate added to neutralise the sulphuric acid. The vinyl benzoate was obtained by fractional distillation, and purified by redistillation. B.pt. of fraction collected, 108°C/30 mm.

In the course of the preparation, a second, large fraction was observed. This fraction, a water-clear liquid, was collected and refractionated through a pear-drop column. B.pt. 81.5°C/30 mm.

In initial preparations by the ester-interchange reaction, commercial vinyl acetate stabilised with copper acetate was used. Later, a mixture of 10 moles freshly distilled vinyl acetate to one mole of stabilised vinyl acetate was used, and finally pure vinyl acetate was used in the preparation.

(c) Commercial sample.

Samples of vinyl benzoate were supplied by Polymer Consultants, Ltd., and used as obtained from the makers.

3.1.2. Ethylidene diacetate.

One mole of acetic anhydride and one mole of vinyl acetate were refluxed for three hours in the presence of 0.5 gm. concentrated sulphuric acid. The

product was isolated by fractional distillation, and redistilled through a short column. B.pt. 80°C/30 mm.

3.1.3. Propene.[56]

65 gm. redistilled n-propyl alcohol, 15 ml. concentrated sulphuric acid, and 35 gm. hydrated aluminium sulphate were placed in a two-litre flask, and gently refluxed. The gas evolved was led in turn through the reflux condenser, an ice-cooled suction flask, and finally two traps immersed in an acetone/"Drikold" freezing mixture at -80°C, where it was collected. When evolution of the gas began to decrease, a further 40 ml. concentrated sulphuric acid were added to the reaction mixture, and heating continued until completion of the reaction.

The condensed propene was transferred to a high-vacuum line, and purified by distillation under high vacuum. The gas was then allowed to evaporate into storage bulbs on the line, where it was kept for further use. No physical constants were measured.

3.1.4. Nitric oxide.

100 ml. 1:1 nitric acid were added to copper turnings. After rejection of the initial gas sample, the gas evolved was collected over water to free it from further traces of nitrogen peroxide. The nitric oxide was then passed through two silica gel tubes,

and thence directly into a storage bulb on the high-vacuum line. No physical constants were measured.

3.1.5. Other compounds.

All other compounds were purchased. Vinyl acetate, ethyl maleate, and cyclohexene were purified by distillation under high vacuum before use.

3.2. Examination of the Vinyl Benzoate Samples and Related Fractions.

Comparison was made of the two vinyl benzoate samples (Section 3.1.1., (a) and (b)) by their infra-red and ultra-violet spectra.

The infra-red spectrum of the vinyl benzoate made by method 3.1.1.(b) (hereafter called the interchange ester) was also compared to the ester obtained by purchase. These two samples were further compared by examination of their vapour-phase chromatograms. The analytical unit used for this purpose was a gas-liquid partition chromatography unit built to conventional design, and employing a 4-foot length of 4 mm. bore tube packed with "Celite 545" containing 20% "Apiezon M" grease.

The second fraction arising in the ester-interchange reaction was also chromatographed, as was the prepared ethylidene diacetate, and comparison of

these two samples again supplemented by infra-red analysis. The molecular weight of the unknown fraction was determined by freezing-point depressions of solutions in nitro-benzene.

3.3. Pyrolysis of Vinyl Benzoate.

A study of the pyrolysis of vinyl benzoate in the gas-phase presented certain aspects which precluded the use of classical gas-phase experimental techniques. The complex breakdown, and the recognised difficulties of preparing the ester in pure form, would clearly obscure, to some degree at least, the meaning of recorded results. The more serious, and limiting, difficulty, however, was the very low volatility of the ester (distillation on a vacuum line was very slow even when the ester was opened to the pump); the ester, therefore, could not be handled in the gas-phase in the normal way. Thus it was decided that an empirical approach would be the most fruitful means of a primary attack upon the problem.

3.3.1. Flow system.

In an initial examination of the pyrolysate of vinyl benzoate, it was desirable to degrade the ester under such conditions that only a small degree of breakdown took place, in an effort to isolate the

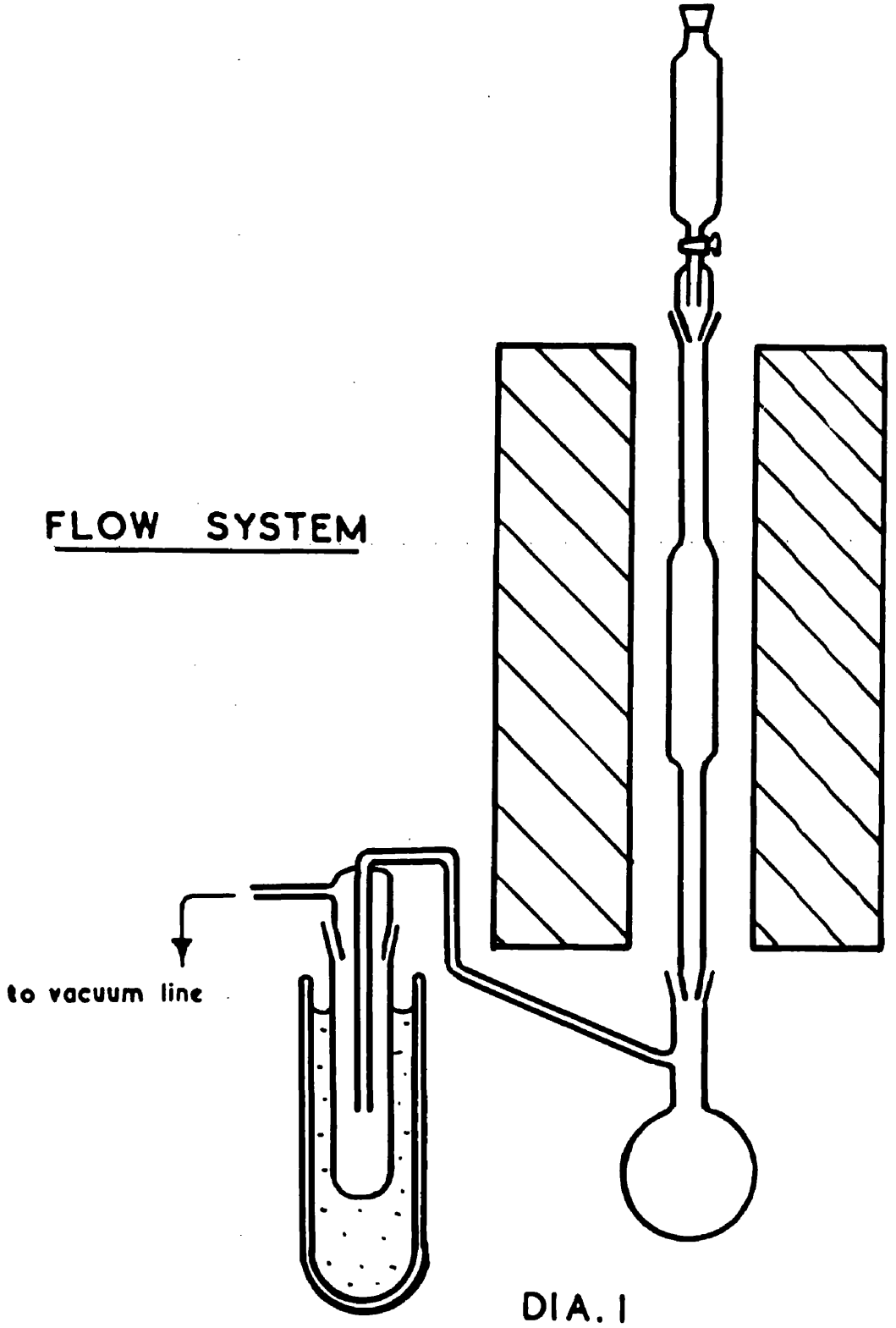
postulated unstable intermediate, benzoylacetaldehyde, from route R/C^1. The apparatus used (Dia. 1) was a modified version of the flow system described by Allan, Forman, and Ritchie.[10] Pyrolysis took place in a Pyrex glass reactor tube, 60 cm. long and 3 cm. diameter over its central 20 cm. length, the tube being supported in a vertical electrically heated furnace. The outlet of the reactor was connected by a ground-glass joint to an all-glass system connected to a high vacuum line, and containing a number of traps in which the pyrolysates were collected. The reactor tube was packed as desired, and the system evacuated, the pyrolysand in the feed container being de-gassed at the same time. Nitrogen was added from a reservoir on the line to give any desired initial pressure. Pressures were measured on a mercury manometer, and the temperature was measured by a chromel-alumel couple placed in a thermocouple pocket situated at the centre of the reactor tube.

The pyrolysates were fractionated under high vacuum, hot-water baths being used to distill off the higher boiling fractions.

3.3.2. Static system.

It was required to devise a system whereby the rate of decomposition of vinyl benzoate in the gas

FLOW SYSTEM



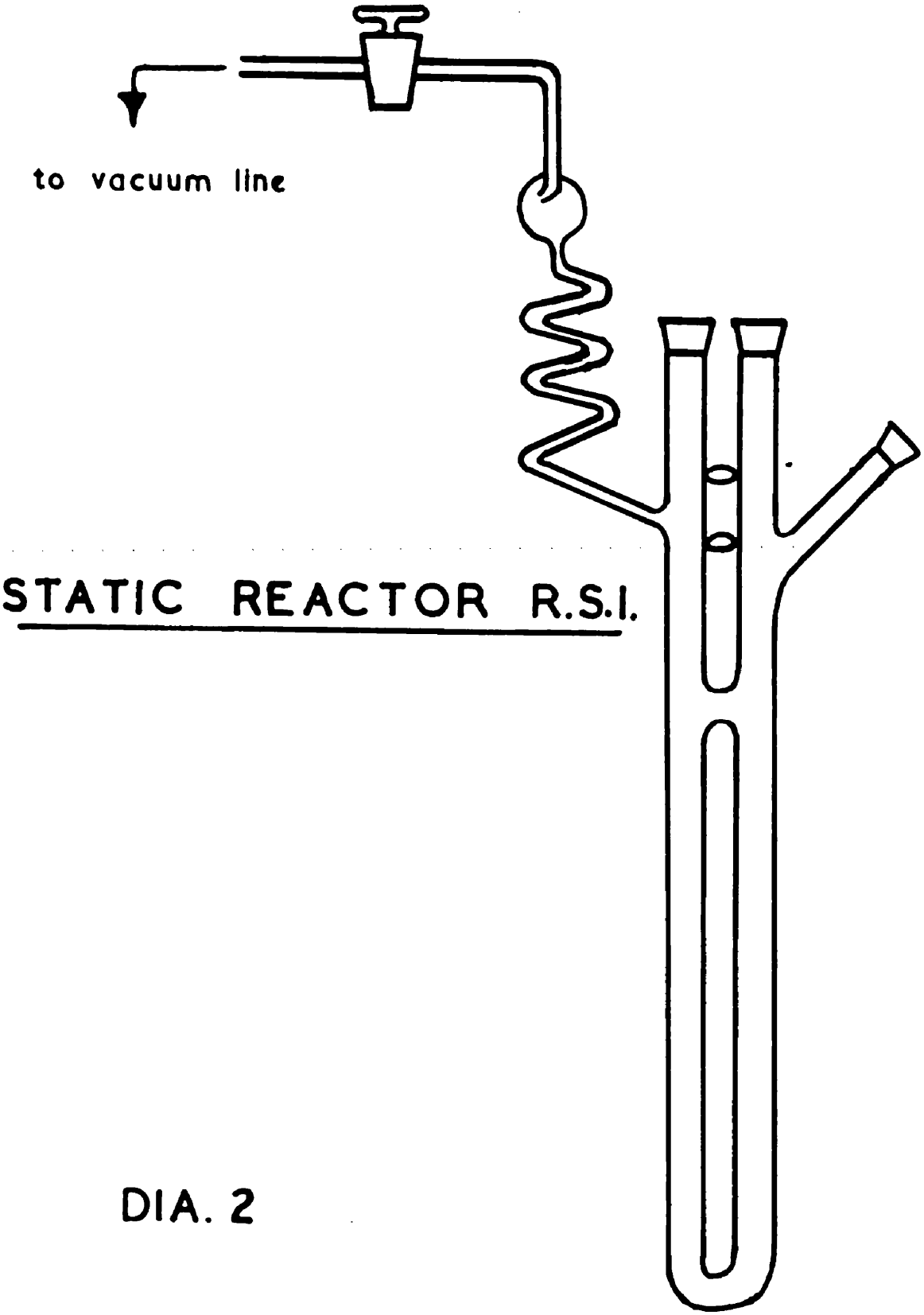
DIA. 1

phase could be conveniently followed under different conditions. While classical experimental techniques could not be applied because of the ester's low volatility, it was evident that some means of following pressure changes in a closed system would provide the best method of tracking the reaction.

Initially the ester was pyrolysed in a simple U-tube attached to a high vacuum line, and the pressures changes followed on a mercury manometer.

While this system yielded the required pressure-time plots, it had certain undesirable features. By examining the areas of carbonisation after a run, it was apparent that pyrolysis was taking place almost solely in that limb attached to the high vacuum line. Moreover, the hot ester, under the vigourous refluxing conditions, tended to be carried out of the reactor altogether and into the adjacent traps. A number of modifications, therefore, were made, and the reactor finally employed is shown in Dia. 2. The arrangement of the reactor and feed container is shown in Dia. 3.

The reactor followed the original design in that it was still essentially a U-tube, fitted at the high vacuum side with a coiled air condenser and splash head. The two limbs of the reactor were joined by a



STATIC REACTOR R.S.I.

DIA. 2

bridge at the top of the reactor to allow smooth diffusion of hot vapours from one limb to the other. The bridge also increased the rigidity of the reactor, and this was further enhanced by sealing two glass beads in between the limbs above the bridge. Reactants were introduced from a container fitted to a side arm, the major volume of which could be isolated as required. Easy access to the limbs could be made from the top of the limbs, which were stoppered ground-glass joints. Each limb of the reactor was 12 mm. diameter, and the length to the bridge was 43 cm.

The volume of the reactor to the bridge was approximately 65 ml., and to the tap above the splash head 130 ml. The volume of the reactor, leads to manometer, and adjacent trap, i.e., the total volume available in the course of a run, was 450 ml. The reactor was placed in a vertical electrically heated furnace, in such a position that the bottom of the vessel coincided with the hot-spot of the furnace, i.e., 45 cm. from the top of the furnace. In the course of a run the furnace was plugged at the bottom, but left open at the top, to encourage steady condensation of the reactants, and so prevent bumping in the column.

Temperature measurement and temperature distribution.

Temperatures in the furnace were measured by a chromel-alumel couple placed at the hot-spot of the furnace, and held at the outside wall of the reactor. The temperature control unit was a manually operated "Sunvic" thermostat. Taking the couple readings from a 0-25 millivoltmeter, the temperature range during the course of a run was $\pm 3^{o}C$. For high temperature work, when a 0-50 millivoltmeter had to be used, the temperature range was $\pm 5^{o}C$.

The temperature distribution in the vertical plane was measured during the course of a run, and is shown in Fig. 1. No detectable variation in temperature could be found across the diameter of the empty furnace tube.

Operation of the static system.

In general operation, the system was set up as indicated in Dia. 3, and a measured volume of pyrolysand placed in the side-arm container. The reactor was then evacuated by means of an oil pump and a two-stage mercury diffusion pump, the pyrolysand being similtaneously de-gassed. Evacuation was normally carried out for a minimum of 30 minutes, but the absolute pressure attained was never measured. The reactor was then cut off from the pumps, but left

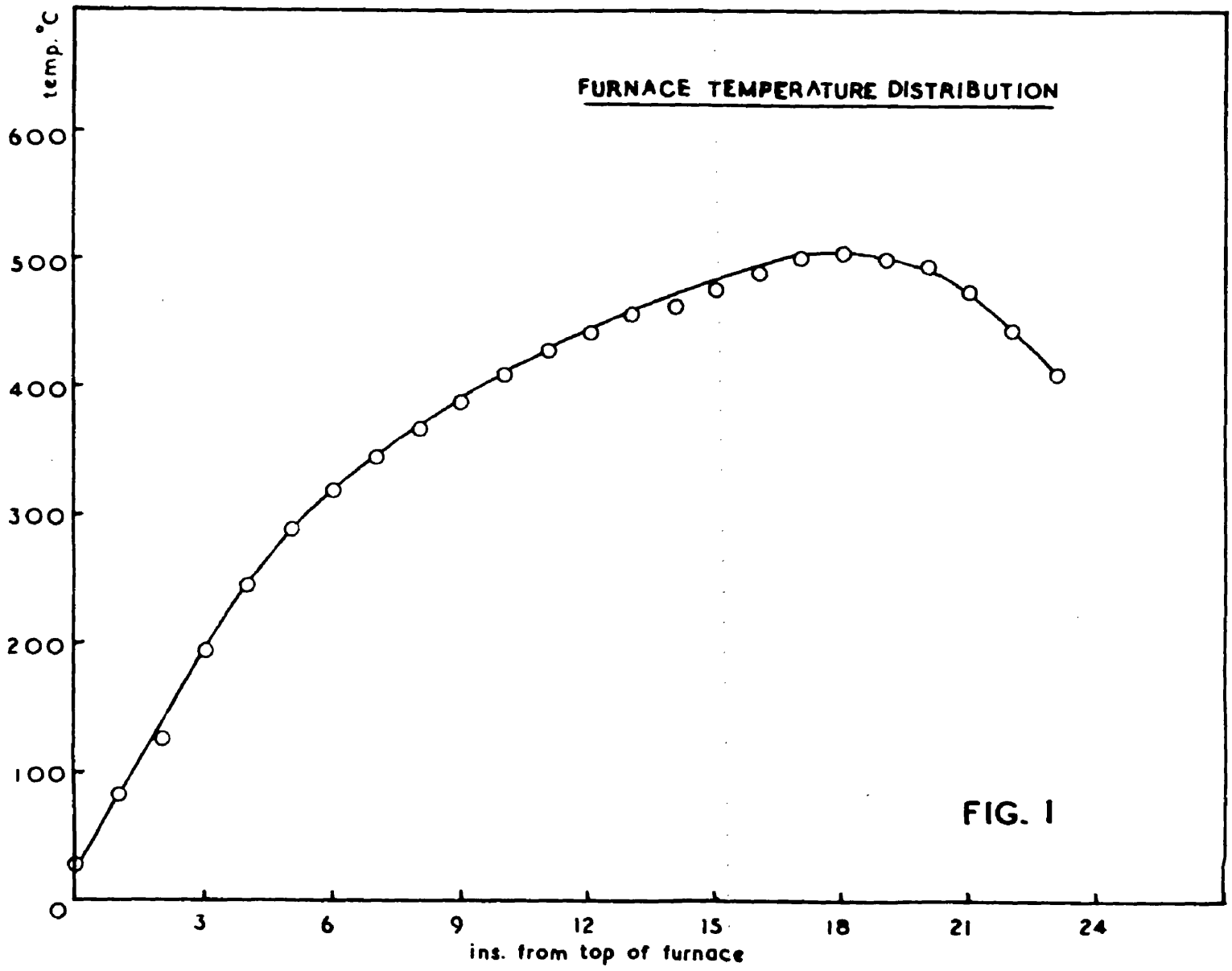

FURNACE TEMPERATURE DISTRIBUTION
temp. °C
600
500
400
300
200
100
0
3
6
9
12
15
18
21
24
ins. from top of furnace

FIG. 1

open to an evacuated 5-litre bulb, and the pyrolysand allowed to drop into the vessel. When this was completed the reactor and a single adjacent trap were isolated from the remainder of the vacuum line and the feed container, and the rate of gas evolution followed by measuring the pressure changes in the system on a simple mercury manometer.

Pressure changes in the system were effected by opening the system to a series of evacuated or gas-filled bulbs. Nitrogen or carbon dioxide were used as inert gases. In the latter case, solid carbon dioxide was allowed to evaporate into an evacuated bulb, and then frozen out in a second trap. Residual gases were pumped off, the procedure repeated, and the gas then stored for use as required.

Nitric oxide and propene were introduced directly from storage bulbs. Small pressures of gases could be conveniently added *via* a capillary tap.

Solid and liquid inhibitors and initiators were either dissolved directly in the pyrolysand, or added in a suitable low-boiling solvent, which was then removed under vacuum.

Co-pyrolysis of vinyl benzoate with its decomposition products (benzoic acid, styrene, and

acetophenone) were carried out by first dissolving the products in the ester, before applying the normal procedure.

The reactor was packed, when required, with glass wool, or "Fibreglass" diamond mat. When the latter was used, it was first heated in a stream of air at 500°C for about an hour to burn off the resin which was impregnated on the surface of the mat.

High vacuum silicone grease was used on all joints which were in contact with the hot pyrolysand. Otherwise "Apiezon" grease was used.

2 ml. pyrolysand were used for each run, unless where otherwise stated. Pyrolysis was carried out at a hot-spot temperature of 520°C, unless where otherwise stated.

Decarbonisation of the reactor.

In an endeavour to minimise changes due to wall effects, a standard procedure was adopted to clean the reactor after a pyrolysis. The condensed reaction products were first washed out with mixed solvents, and the tube then decarbonised for two hours at 540°C, air being drawn through the vessel by a water-pump.

3.3.3. Test-tube reactor.

In order to examine certain suspected diffusion effects in the static apparatus described above, it

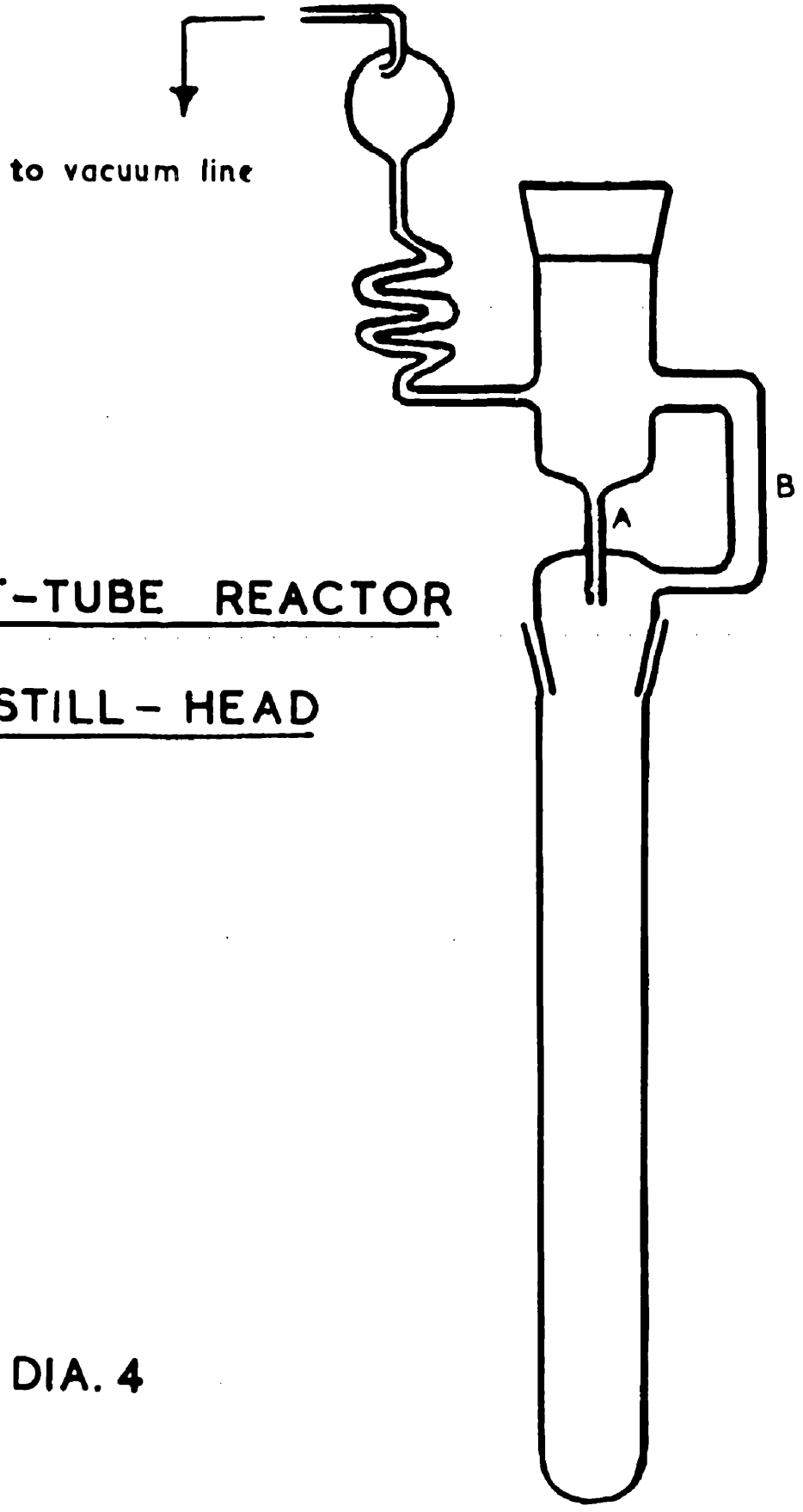
was decided to use a sequence of still-heads in conjunction with a simple test-tube reactor.

In practice, three test-tube reactors similar to that shown in Dia. 4, but of varying diameter, were used. The length of each reactor was 46 cm., and the diameters used were 1.0 cm., 2.0 cm., and 3.5 cm.

A number of still-heads were used with these reactors, all of the general design shown in Dia. 4. In use, the feed container was attached to the ground-glass joint at the top of the still-head. The pyrolysand dripped through the centre tube, A, which was of standard diameter 0.4 cm., and thence into the reactor attached to the lower ground-glass joint. The reflux and the evolved gases passed through the side arm, B, which had a varying diameter, viz., 0.5 cm., 1.5 cm., or 2.0 cm. The take-off was then led to the standard air condenser and splash head, as before.

Care had to be taken in applying a thin even film of silicone grease to the joint at the top of these reactors, due to a tendency for the hot refluxing liquid to wash the grease down and cause leaks from atmosphere.

In operation, the same general procedures were applied to this system as had served in the original



TEST-TUBE REACTOR and STILL-HEAD

DIA. 4

static apparatus. A pyrolysis carried out in a reactor coated with silica was accomplished by dispersing some silicone grease in acetone, and spreading the dispersion in a thin film over the surface of the reactor. The solvent was then quickly evaporated, the tube evacuated, and heated at 500°C for one hour.

3.3.4. Gas analysis.

The analysis of gas samples was carried out in a Sleigh[57] gas analysis unit, a unit which can be used for small samples up to a maximum of 9 ml. The gases were transferred from the static system to a detachable gas sample tube by means of a Toepler pump, and hence to the Sleigh unit.

3.4. Pyrolysis of Vinyl Acetate.

A short comparitive examination of the pyrolysis of vinyl acetate was made. It was found necessary to work at temperatures of up to about 950°C, and the reaction vessel employed, therefore, was made of "Vitreosil". The reactor was of the simple test-tube type described above, of length 46 cm., and diameter 2.0 cm., and was fitted at the top with a B.24 ground-glass joint. The top of the reactor was connected directly to the manometer by a length of capillary

glass tubing attached to a fitting ground-glass joint, no traps being included in the closed system during a pyrolysis. The approximate volume of the reactor was 145 ml., and the volume of the joining connections and leads was less than 10% of the reactor volume.

Vinyl acetate vapour was introduced into the reactor in one of two ways; either by allowing the ester to distill into the closed system *via* a capillary tap from a storage trap containing liquid vinyl acetate, or by opening the capillary tap to a bulb containing vinyl acetate vapour. When working with nitrogen, the gas was either added after the vinyl acetate, or as a mixture of known composition with the vinyl acetate vapour.

Very small silica chips (diameter ca. 2 mm.) were used when required to pack the vessel, giving a very large increase in the surface/volume ratio in the reactor.

Iodine was added during the course of a run by dropping a small pellet into the reactor from a "spoon" inserted into a special still-head used for this purpose.

Nitric oxide and *cyclo*hexene were added to the system immediately before the ester vapour *via* the capillary tap.

In all other respects the general techniques already described for the studies of vinyl benzoate were applied. As the temperature was measured on a 0-50 millivoltmeter, the estimated accuracy of control was $\pm 5^{o}C$.

4. RESULTS.

4.1. Examination and Comparison of Vinyl Benzoate Samples.

The large second fraction observed in the ester-interchange reaction, on refractionating through a short column, distilled at 80°C/30 mm. Distillation at atmospheric pressure resulted in decomposition over the range 168-180°C. The resulting vapours gave a precipitate with 2:4-dinitrophenylhydrazine, identified as the derivitive of acetaldehyde (m.pt. 157-159°C; mixed m.pt. 158-160°C; lit. 161-162°C). The product, thought to be ethylidene diacetate, which decomposes smoothly on distillation at atmospheric pressure to give acetic anhydride and acetaldehyde, had a molecular weight of 141, measured in nitro-benzene (ethylidene diacetate 146). Comparison of the infra-red spectra of the unknown product and a prepared sample of ethylidene diacetate (Fig. 3) confirmed that the former was ethylidene diacetate, arising from the addition of acetic acid to vinyl acetate. The production of ethylidene diesters in the ester-interchange reaction has been observed previously.[58]

The vapour-phase chromatogram of the ester-interchange vinyl benzoate was found to have two peaks,

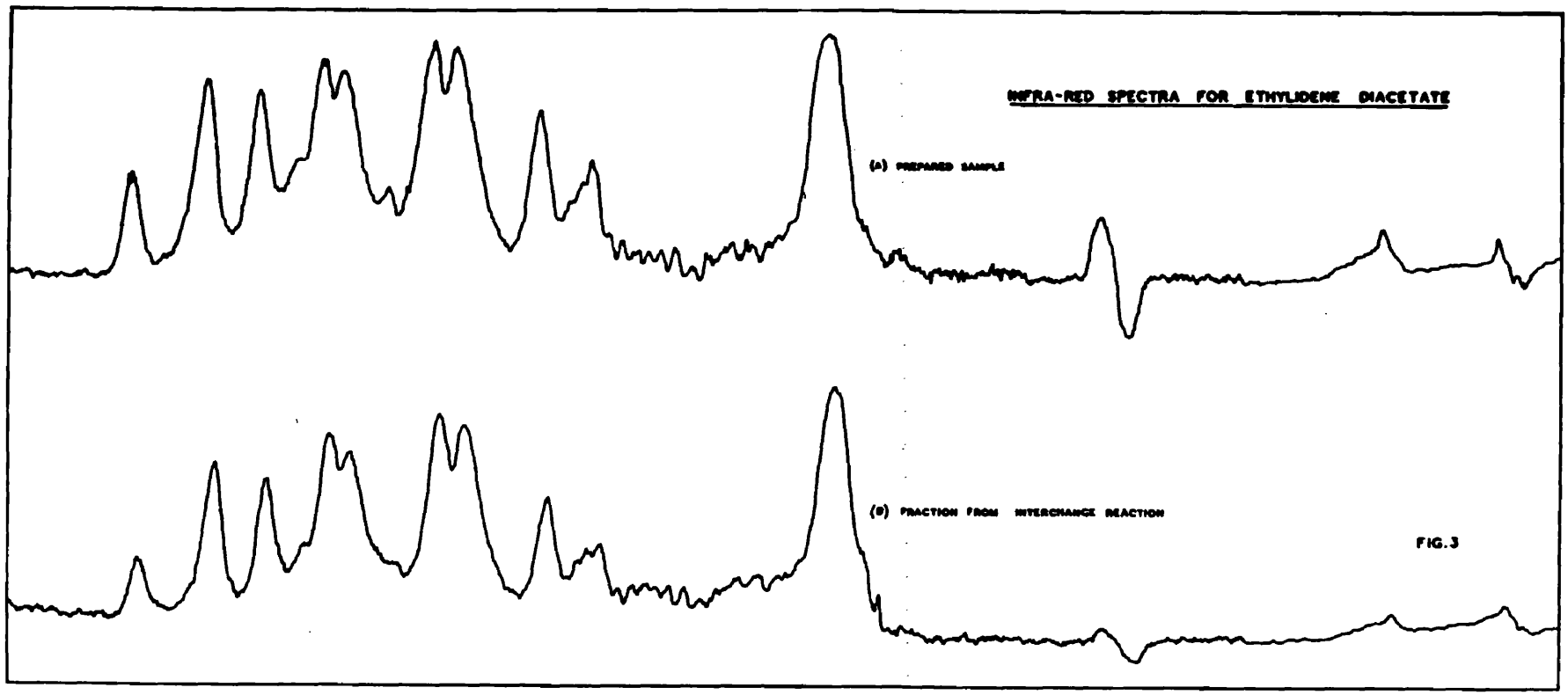

INFRA-RED SPECTRA FOR ETHYLIDENE DIACETATE
(a) PREPARED SAMPLE
(b) FRACTION FROM INTERCHANGE REACTION

FIG. 3

and by comparison to a standard the second peak was seen to correspond to ethylidene diacetate (Fig. 2). The vinyl benzoate supplied by Polymer Consultants, Ltd. also gave a two-peak chromatogram with almost identical retention times to the prepared ester. In both cases the diester was estimated from the peak areas as constituting 5-10% of the sample. This figure could not be substantially reduced by further fractionation without subjecting the ester to long periods of reflux.

Initial yields of "purified" vinyl benzoate in the ester-interchange reaction were 7-10%. These yields were found to improve by reducing the quantity of copper salt inhibitor in the vinyl acetate, and latterly, by using uninhibited vinyl acetate, yields of 20-25% vinyl benzoate were obtained, without any polymerisation of the reactants or products being apparent.

By the pyrolysis of ethylene dibenzoate, it was found that a yield of 40% vinyl benzoate could be obtained after a 6-hour pyrolysis of 50 gm. starting material. The product had a pale green colouration. No further examination of this product was made. Samples of vinyl benzoate prepared by this route have already been estimated[10] to contain up to 7%

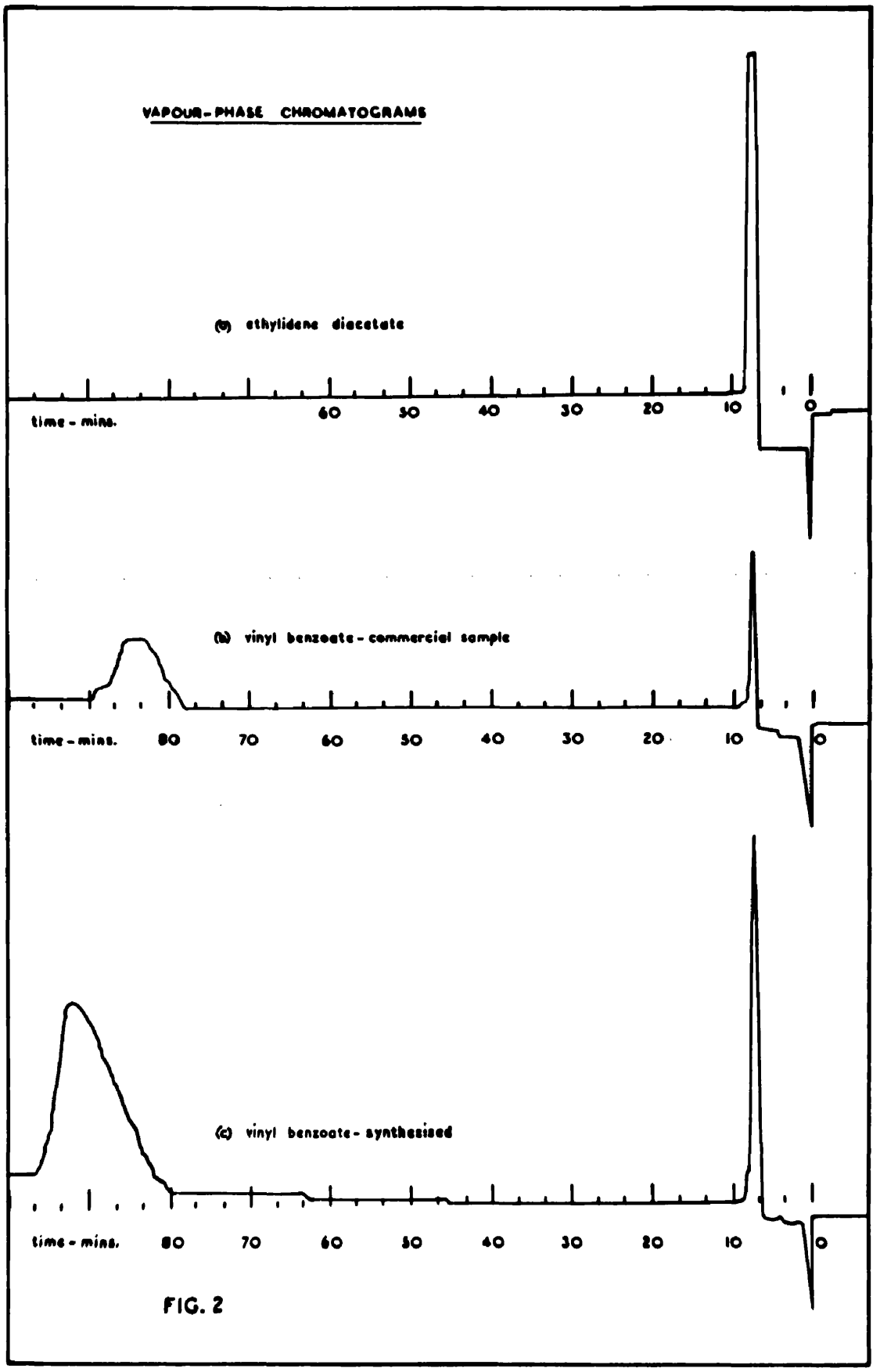

VAPOUR-PHASE CHROMATOGRAMS
(a) ethylidene diacetate
time - mins.
60
50
40
30
20
10
0
(b) vinyl benzoate - commercial sample
time - mins.
80
70
60
50
40
30
20
10
0
(c) vinyl benzoate - synthesised
time - mins.
80
70
60
50
40
30
20
10
0

FIG. 2

acetophenone in addition to smaller quantities of other degradation products.

4.2. Pyrolysis of Vinyl Benzoate. - Flow System.

The ester pyrolysed in the flow system was prepared by the pyrolysis of ethylene dibenzoate.

In unpacked reactors, no breakdown of the ester was apparent at 460°C, even in nitrogen atmospheres of up to 500 mm. pressure. By introducing glass helices or glass wool packing, some degree of breakdown took place (apparent by the carbonisation of the reactor, and discolourisation of the pyrolysand).

Although a detailed examination of the pyrolysates was not made, acetophenone and benzoic acid were readily identified, the former by its 2:4-dinitrophenylhydrazone, the latter by mixed melting point. A specific search was made for carbonyl fractions corresponding to benzoylacetaldehyde, but none could be detected. Only acetophenone could be found in the lighter fractions, and the residue, after distillation on an oil bath under high vacuum, consisted mainly of benzoic acid, along with a small quantity of polymeric material.

4.3. Pyrolysis of Vinyl Benzoate. - Static System.

The investigations outlined below were carried out using ester-interchange vinyl benzoate, i.e., vinyl benzoate containing ethylidene diacetate, with the exception of specifically mentioned cases.

4.3.1. Pyrolysis in a clean reactor.

A typical pressure-time plot obtained for vinyl benzoate, using a clean reactor, is shown in Fig. 4.

The main feature of the reaction was the auto-catalytic nature of the decomposition, i.e., the rate of gas evolution was found to increase with time. In the course of the reaction, a steady maximum value was approached, generally being reached after about 50-60 minutes, after which the rate slowed down fairly rapidly in the later stages of the pyrolysis. (This maximum rate value will be often referred to in the results stated hereafter, being taken as the characteristic value of any particular run).

If, during the course of a run, the pressure was quickly decreased by removing the gaseous reaction products, but retaining the refluxing liquids, a strongly marked decrease in rate was observed. Thus a decrease in pressure from 452 mm. to 17 mm. led to a rate decrease from about 7 mm./min. to 1 mm./min., after which the rate again increased with time.

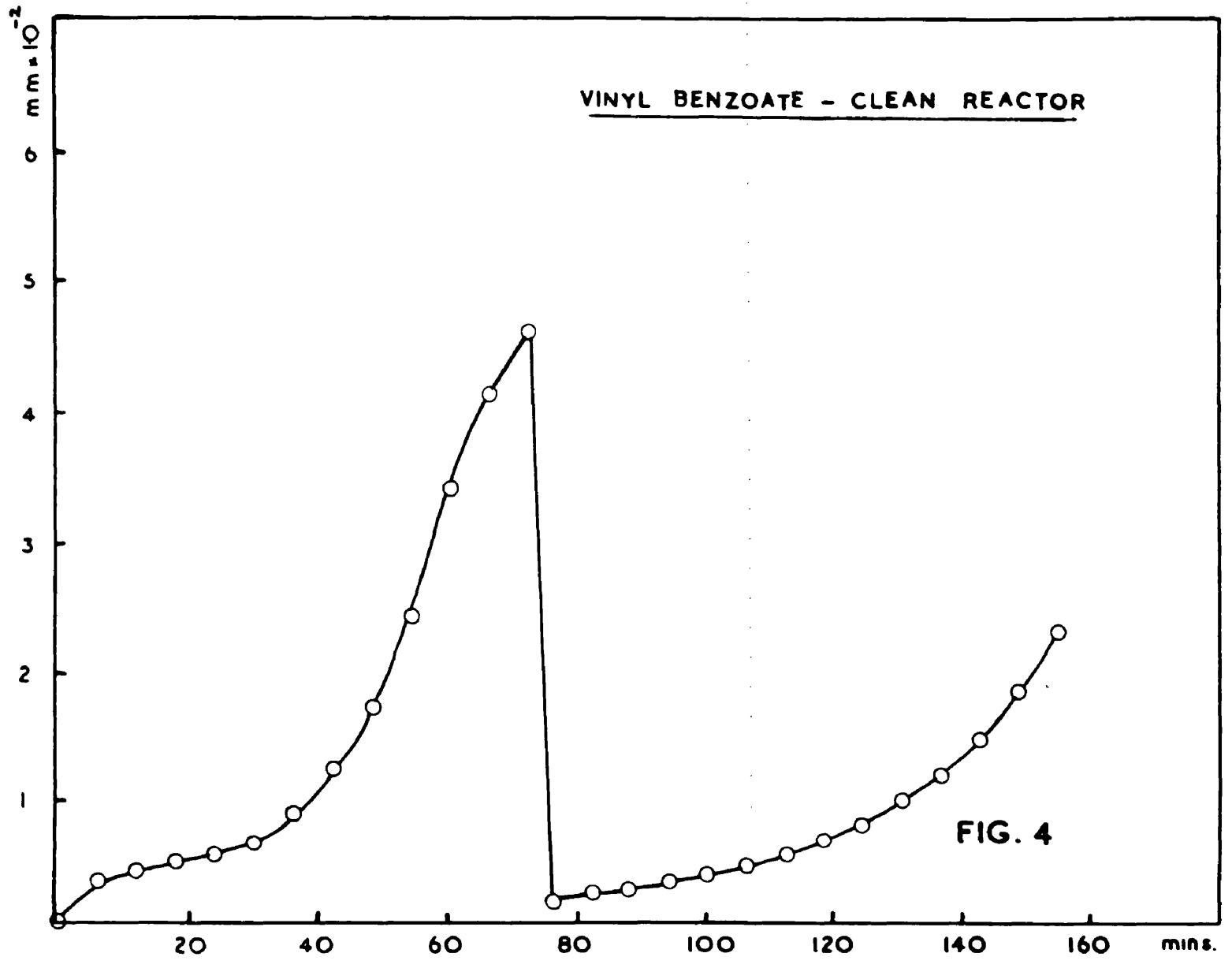

VINYL BENZOATE - CLEAN REACTOR
$M \times 10^{-2}$
6
5
4
3
2
1
20
40
60
80
100
120
140
160
mins.

FIG. 4

The first three to four minutes of the decomposition were characterised by a sharp, initial pressure rise of about 50-100 mm. pressure, which then rapidly slowed down before the autocatalytic nature of the reaction began to take effect. In one run, a "Drikold"/acetone trap was attached to the line after the initial pressure rise had taken place.

A small quantity of liquid was frozen out, from which was obtained a 2:4-dinitrophenylhydrazone, identified as that of acetaldehyde (m.pt. 156-159°C; mixed m.pt. 157-159°C; lit. 161-162°C). A standard procedure was adopted in later runs, whereby after the initial pressure rise had taken place, the pressure was reduced again to a low value (usually about 10 mm.), and the run subsequently followed as usual.

4.3.2. Pyrolysis in a carbonised reactor.

Fig. 5 shows plots obtained in successive runs without cleaning the reactor between each run, i.e., without removing either the deposited carbonaceous film, or the condensed reaction products from previous runs (although as much as possible of the products were removed by pumping while the vessel was raised to 500°C).

With successive pyrolyses, the decomposition rate

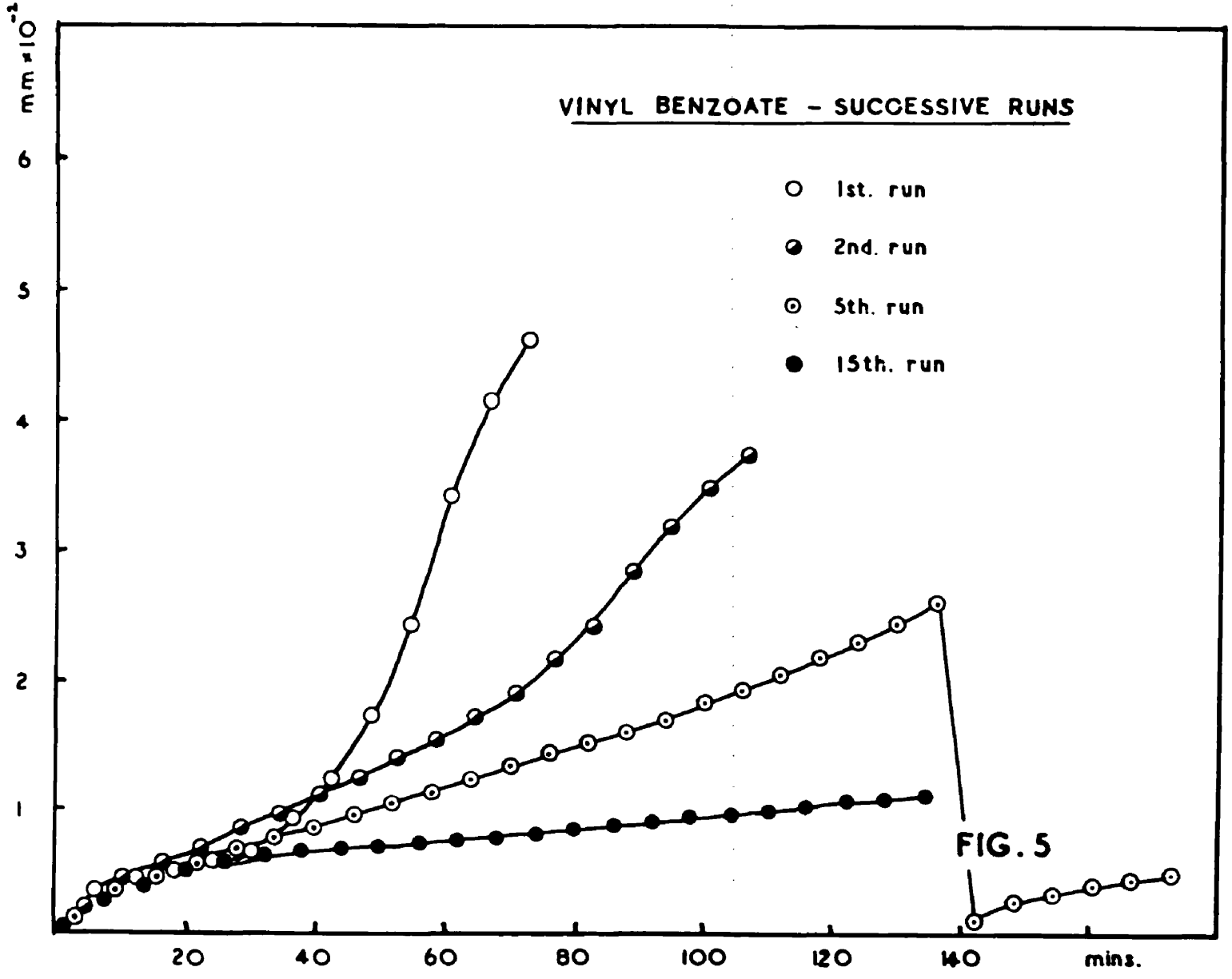

VINYL BENZOATE - SUCCESSIVE RUNS
1st. run
2nd. run
5th. run
15th. run
mm x 10⁻²
6
5
4
3
2
1
20
40
60
80
100
120
140
mins.

FIG. 5

was observed to fall markedly. The rate decrease was particularly severe in the early stages of a series of runs. After about 10 successive runs, a steady rate value was approached. In the series graphed in Fig. 5, after only one carbonisation, the maximum rate value was reduced from 17 mm./min. to 8 mm./min.; after 5 runs, the rate at 60 mins. was ca. 1.5 mm./min., and after 15 runs, the rate at 60 mins. was ca. 0.75 mm./min.

Although only one run was required to cause a halving of the reaction rate, as indicated above, carbonisation after only one run was very light, and was situated almost completely over the bottom six inches of the reactor. As successive runs were carried out, the total carbon deposits became very heavy, but were still contained in the bottom half of the reactor. The deposition of benzoic acid was also noticeable, even after as little as two runs. The acid generally condensed out on the walls of the air condenser during evacuation of the dirty reactor, and in the course of the following run was washed into the reaction vessel by the refluxing liquors.

In the course of a series of runs the autocatalytic effect was greatly reduced, although still present, as could be demonstrated by a reduction in pressure.

Thus, in the 5th. run of the series shown, a reduction in absolute pressure from 253 mm. to 10 mm. caused a fall in the rate from ca. 2.5 mm./min. to ca. 1.25 mm./min.

On washing and decarbonising the reactor after a series of runs, a pressure-time plot characteristic of the clean reactor was obtained immediately.

4.3.3. Reproducibility of decomposition rates in decarbonised reactors.

Many runs were carried out in a "clean" reactor, i.e., one free of carbon deposits and reaction products. It was found that the measured rates were reproducible, within experimental error, over a short period of time, but the pressure-time curves obtained from any one reactor over a period of months tended to drift.

Fluctuations in the plots were greatest in new glass, when rates tended generally to be high, but there did appear to be a seasoning effect which was particularly apparent in the initial 10-20 runs using a new reactor.

One visible change was observed in the nature of the walls of the reactor in the course of time. Very small quantities of silicone grease were gradually washed into the reactor during pyrolysis, as the hot liquors came into contact with the stoppers at the

top of the vessel. A white film of silica was deposited evenly over the walls of the reactor, and this could not be removed completely by any of the normal cleaning agents.

In the early life of a reactor, the time of decarbonisation affected the maximum rate obtained in the succeeding run, up to a cleaning time of as great as five hours. It was never found possible after the early runs in a new vessel to attain maximum rates equivalent to those in new glass, even with the most stringent cleaning procedure.

To overcome these difficulties, the same reactor (R.S.1., Dia. 2) was used continually, except in those cases where specific mention is made of a different vessel. After seasoning, the rate fluctuations became so small that any significant change during a pyrolysis could be readily detected. The cleaning procedure already described (Section 3.3.2.) was found to be satisfactory. Blank runs were carried out at regular intervals to ensure a continuous check on the pyrolytic rate being measured.

4.3.4. Effect of inert gases.

The effect of adding nitrogen and carbon dioxide to the system in the course of a run is shown in Figs. 6 and 7. The addition of 129 mm. nitrogen

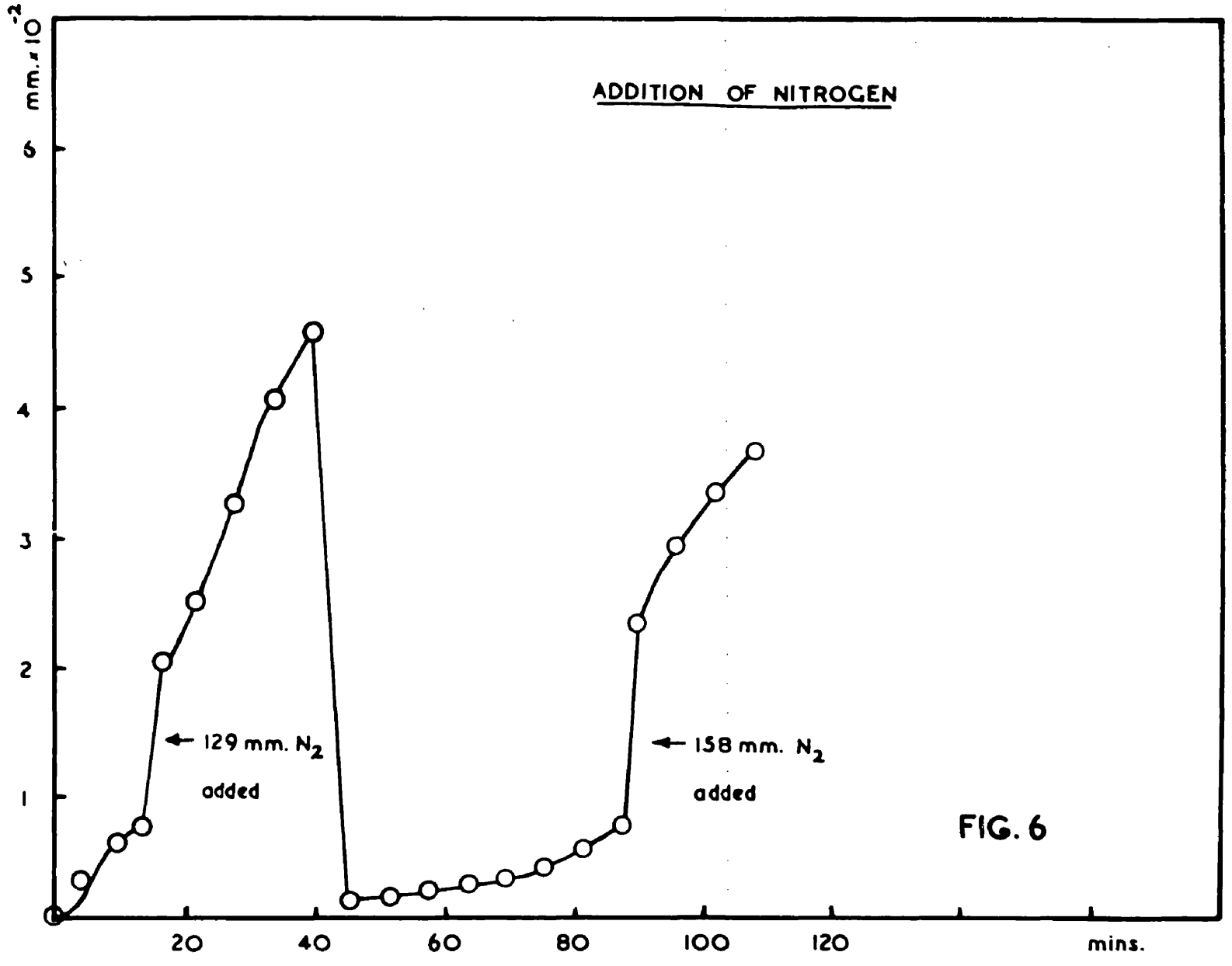

ADDITION OF NITROGEN
mm. x 10^-2
6
5
4
3
2
1
129 mm. N2
added
158 mm. N2
added
20
40
60
80
100
120
mins.

FIG. 6

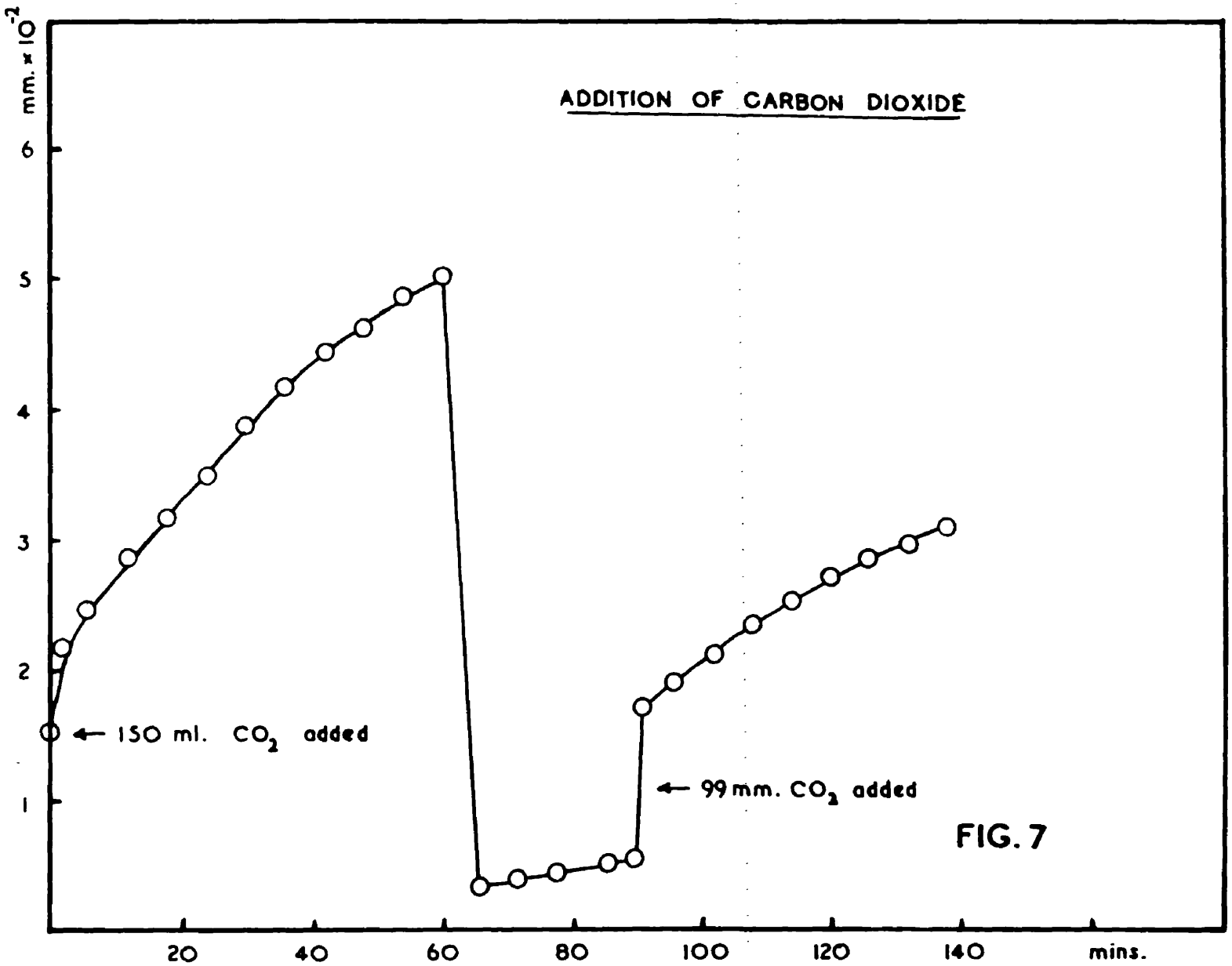

ADDITION OF CARBON DIOXIDE
mm. x 10⁻²
6
5
4
3
2
1
← 150 ml. CO₂ added
← 99 mm. CO₂ added
20
40
60
80
100
120
140
mins.

FIG. 7

gave an immediate rate increase from 3 mm./min. to 9 mm./min. At a later stage in the reaction, a similar addition of 158 mm. nitrogen increased the rate from 3 mm./min. to 10 mm./min. (Fig. 6). The maximum rate value was ca. 15 mm./min., of the same order as the blank run.

Similar effects were obtained using carbon dioxide as an inert atmosphere (Fig. 7). On adding 150 mm. carbon dioxide to the system prior to commencing the run, it was observed that, following the normal very sharp pressure increase in the early stages of the reaction, the maximum rate value was reached almost immediately, being about 17 mm./min., again similar to the blank, the rate then gradually decreasing. Addition of carbon dioxide at a later stage in the reaction, following the removal of most of the gases from the system, again gave an immediate rise in rate, 99 mm. carbon dioxide causing a rate increase from 3 mm./min. to 7 mm./min.

4.3.5. Co-pyrolysis with degradation products.

The addition of benzoic acid in sufficient quantity was found to cause a decrease in the rate of gas evolution (Fig. 8). While ester containing 2% benzoic acid showed no deviation from the blank run, the addition of 5% acid to the pyrolysand caused a

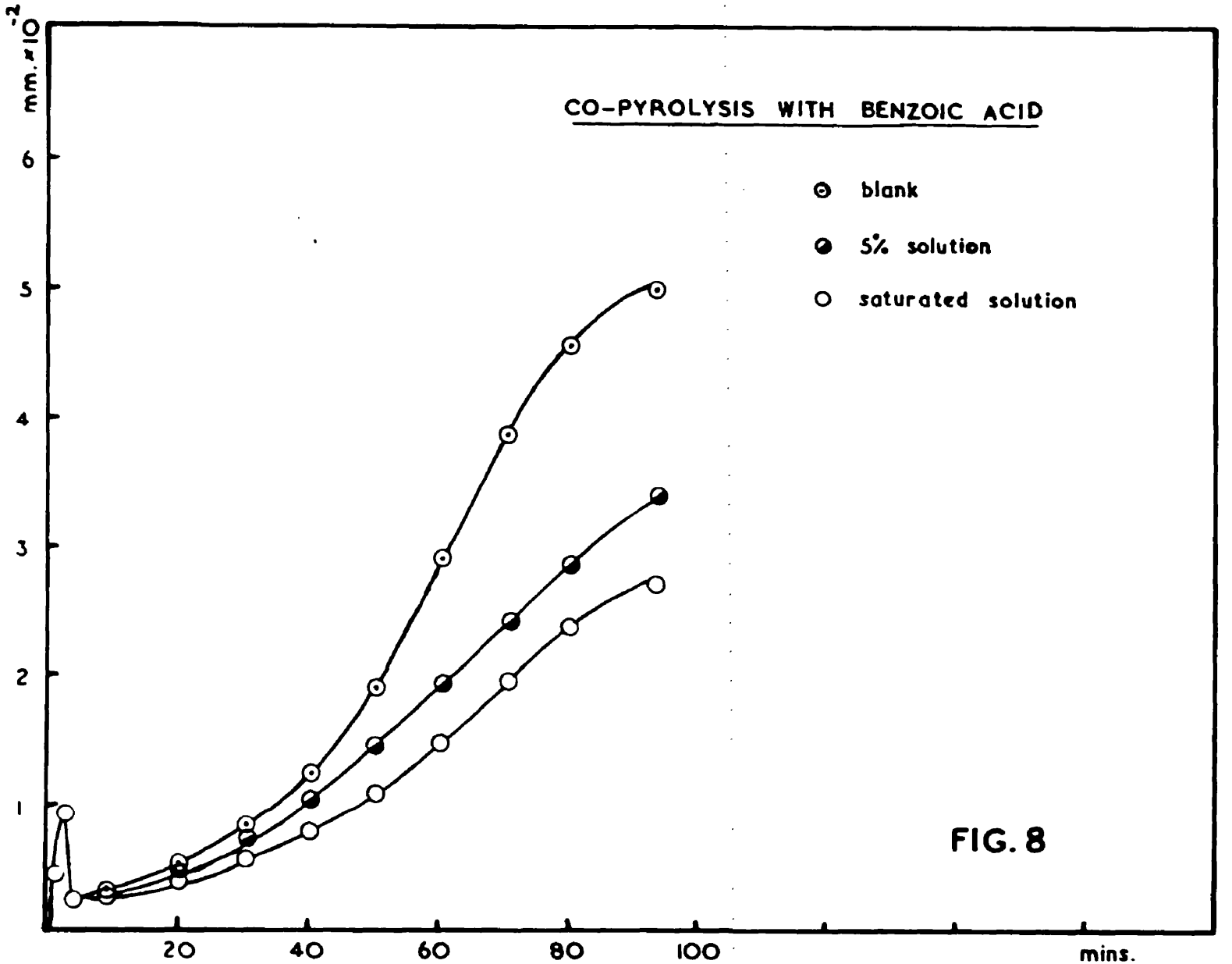

CO-PYROLYSIS WITH BENZOIC ACID
blank
5% solution
saturated solution
mm. x10^-2
6
5
4
3
2
1
20
40
60
80
100
mins.

FIG. 8

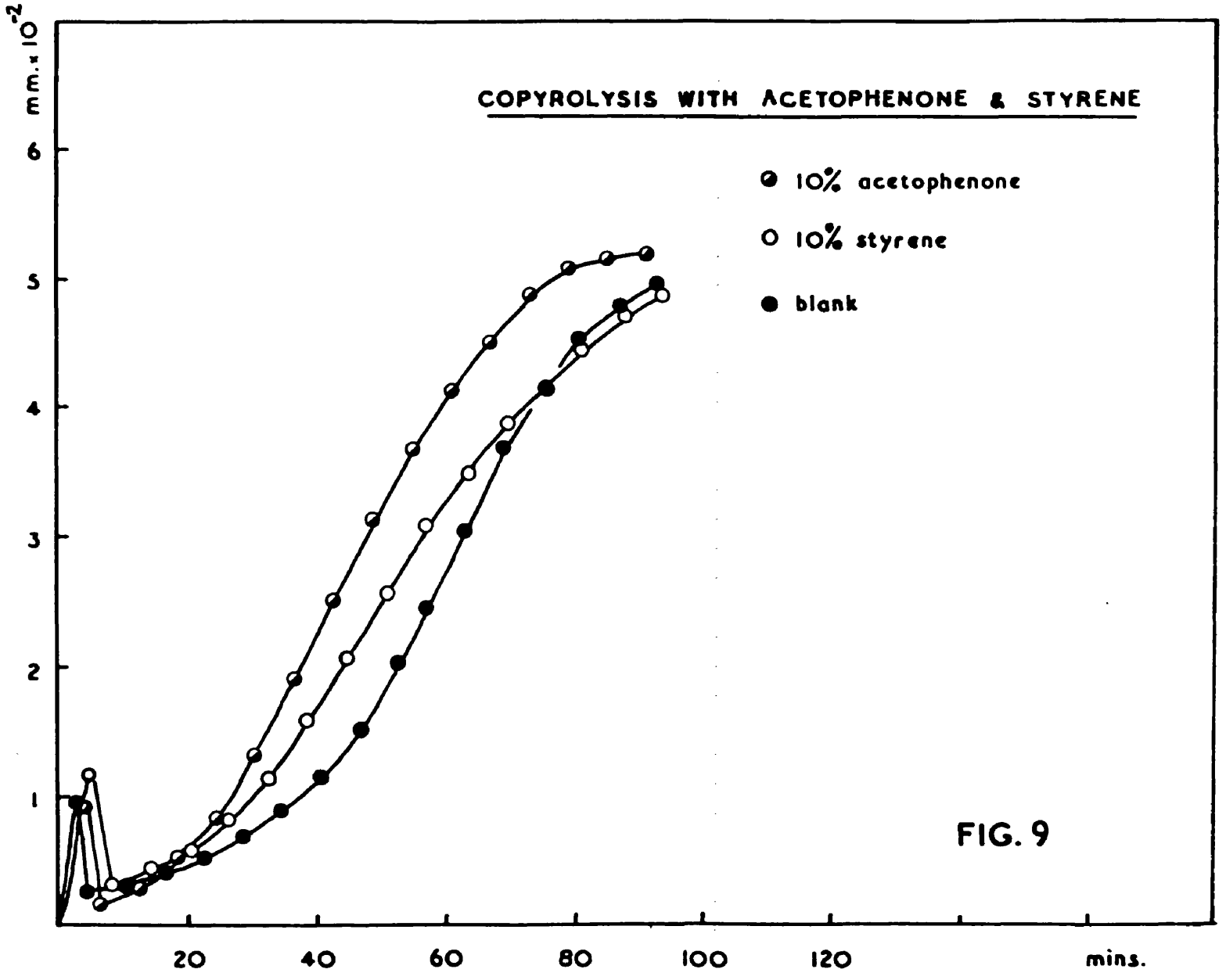

COPYROLYSIS WITH ACETOPHENONE & STYRENE
10% acetophenone
10% styrene
blank
m.m. x 10^-2
1
2
3
4
5
6
20
40
60
80
100
120
mins.

FIG. 9

fall in the maximum rate value from 10 mm./min. to 5 mm./min. Co-pyrolysis of the ester with 10% acid and with a saturated solution, did not cause any further depressions in the rate, the rate maxima recorded being 5 mm./min. with 10% acid, and 6 mm./min. with the saturated solution.

Co-pyrolysis with 10% acetophenone and 10% styrene yielded rates similar to those of the pure ester (Fig. 9).

4.3.6. Rate variation with initial ester concentration.

Plots for a number of runs in which the initial charge of ester was varied are shown in Fig. 10. The maximum rate value reached was found to vary up to a charge of about 3 ml. ester. Moreover, the pressure dependance of the reaction became much more pronounced as the feed volume was increased. For an initial charge of 1 ml. ester, the ratio of initial rate/maximum rate was 1:3. For 3 ml. ester or more, this ratio was raised to 1:10; i.e., in the range 1 ml.-4 ml. pyrolysand, the rates in the early stages of the reaction were of the same order, but the maximum rates were altered by a factor of 3.

Using larger volumes of ester, it was found difficult to introduce pressure changes without some of the ester being carried out of the reactor. It

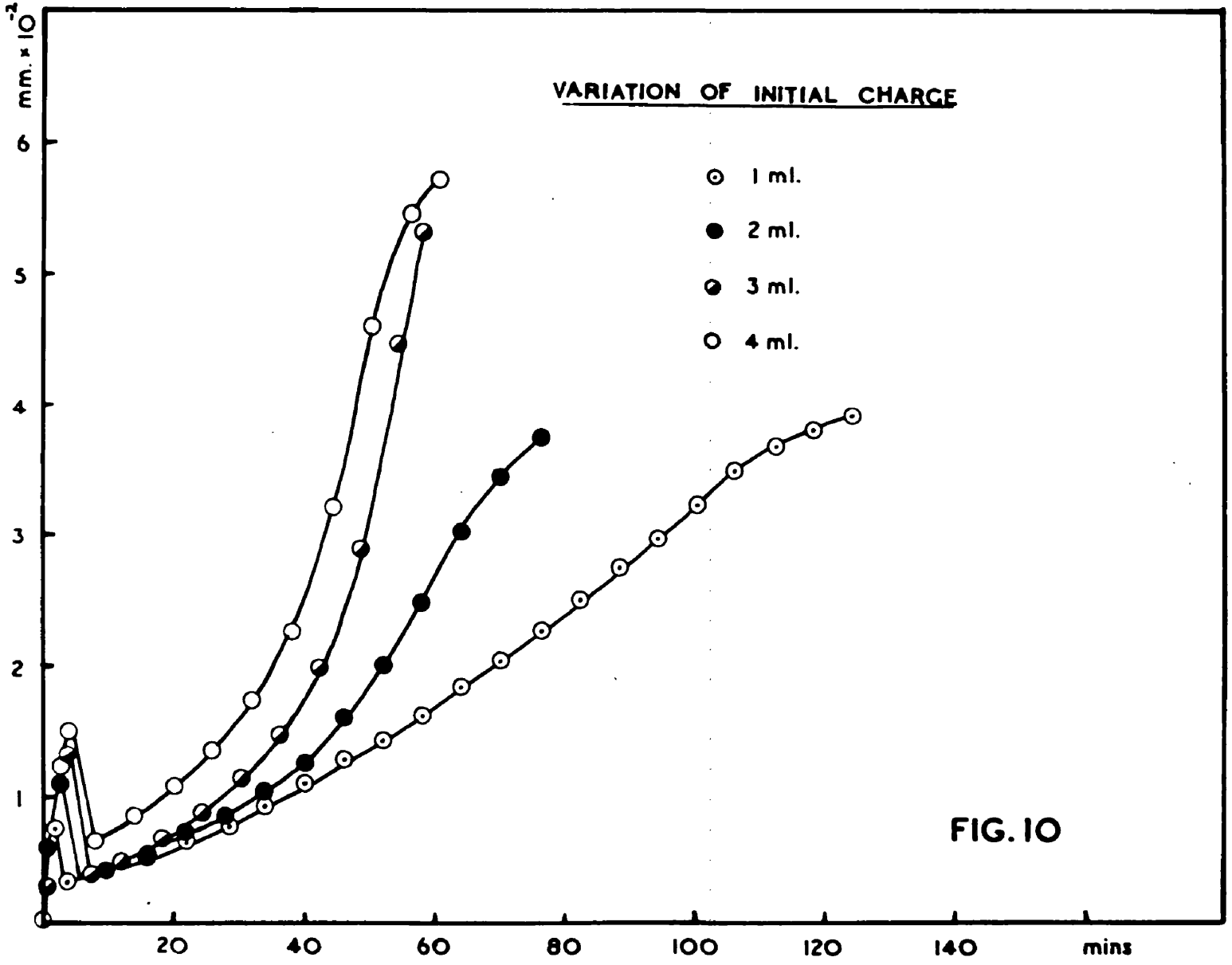

VARIATION OF INITIAL CHARGE
1 ml.
2 ml.
3 ml.
4 ml.
mm. x 10⁻²
6
5
4
3
2
1
20
40
60
80
100
120
140
mins

FIG. 10

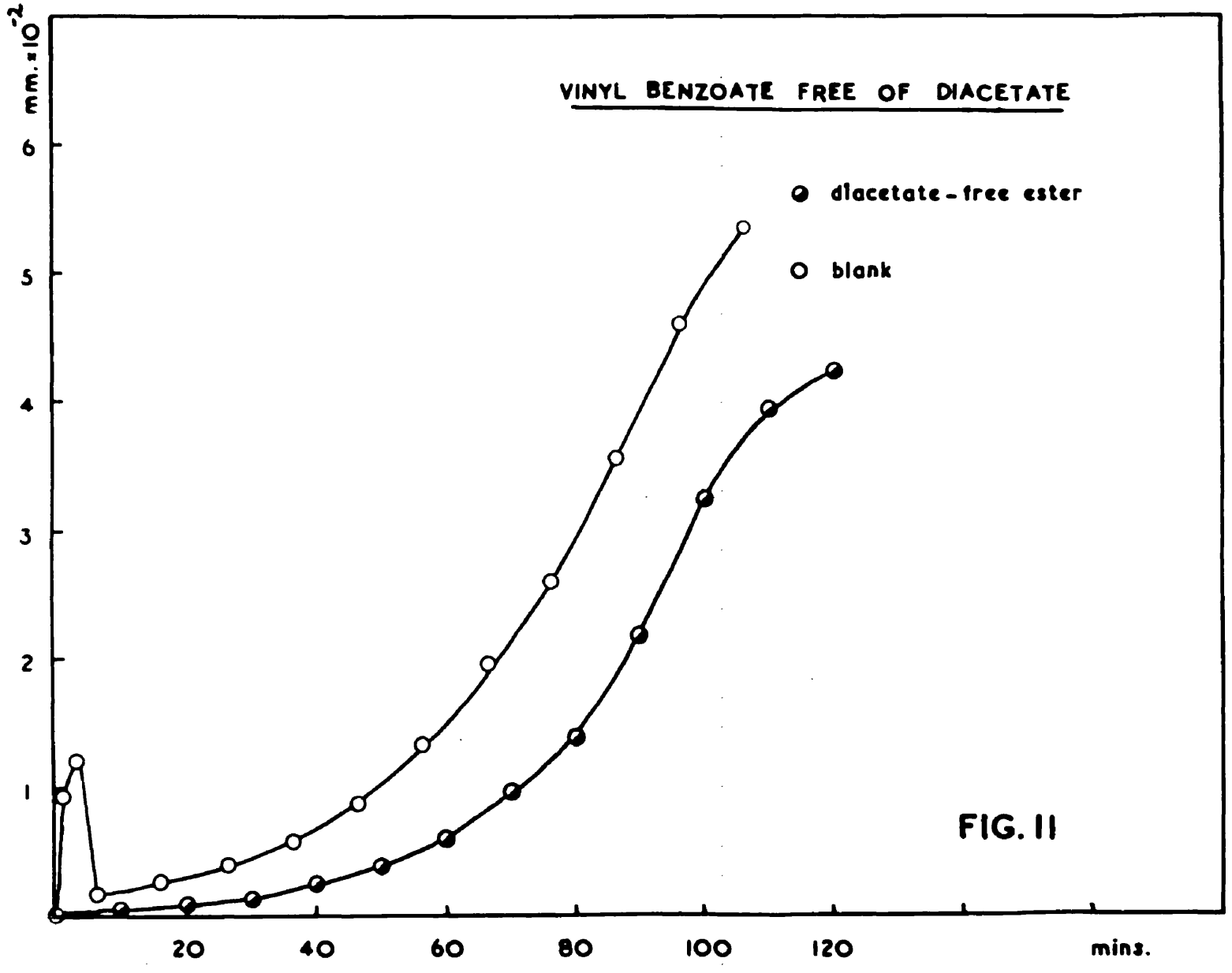

VINYL BENZOATE FREE OF DIACETATE
diacetate-free ester
blank
mm. x 10^-2
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 11

was also more difficult to control the temperature of the system when working with larger quantities of liquid. A convenient compromise was reached by using 2 ml. ester in those runs where a comparitive rather than an absolute rate was required. Such a volume gave a plot which was clearly pressure-dependant, while at the same time being reasonably easy to manipulate.

4.3.7. Pyrolysis in the absence of ethylidene diacetate.

A sample of vinyl benzoate prepared by the pyrolysis of ethylene dibenzoate (Section 3.1.1.), and therefore free of ethylidene diacetate, gave an identical maximum rate value (11 mm./min.) as that of the corresponding blank run with ester-interchange vinyl benzoate, although taking about 20 minutes longer to reach the maximum value (Fig. 11).

4.3.8. The effect of free-radical inhibitors and initiators.

A number of runs were carried out, in carbonised tubes, in the presence of the following free-radical inhibitors and initiators :-

0.1% hydroquinone
0.1% benzoquinone
0.1% toluquinone
0.1% azodicyclohexanecarbonitrile
0.1% benzoyl peroxide

No changes in the reaction rate were observed. The initial pressure rise was not altered.

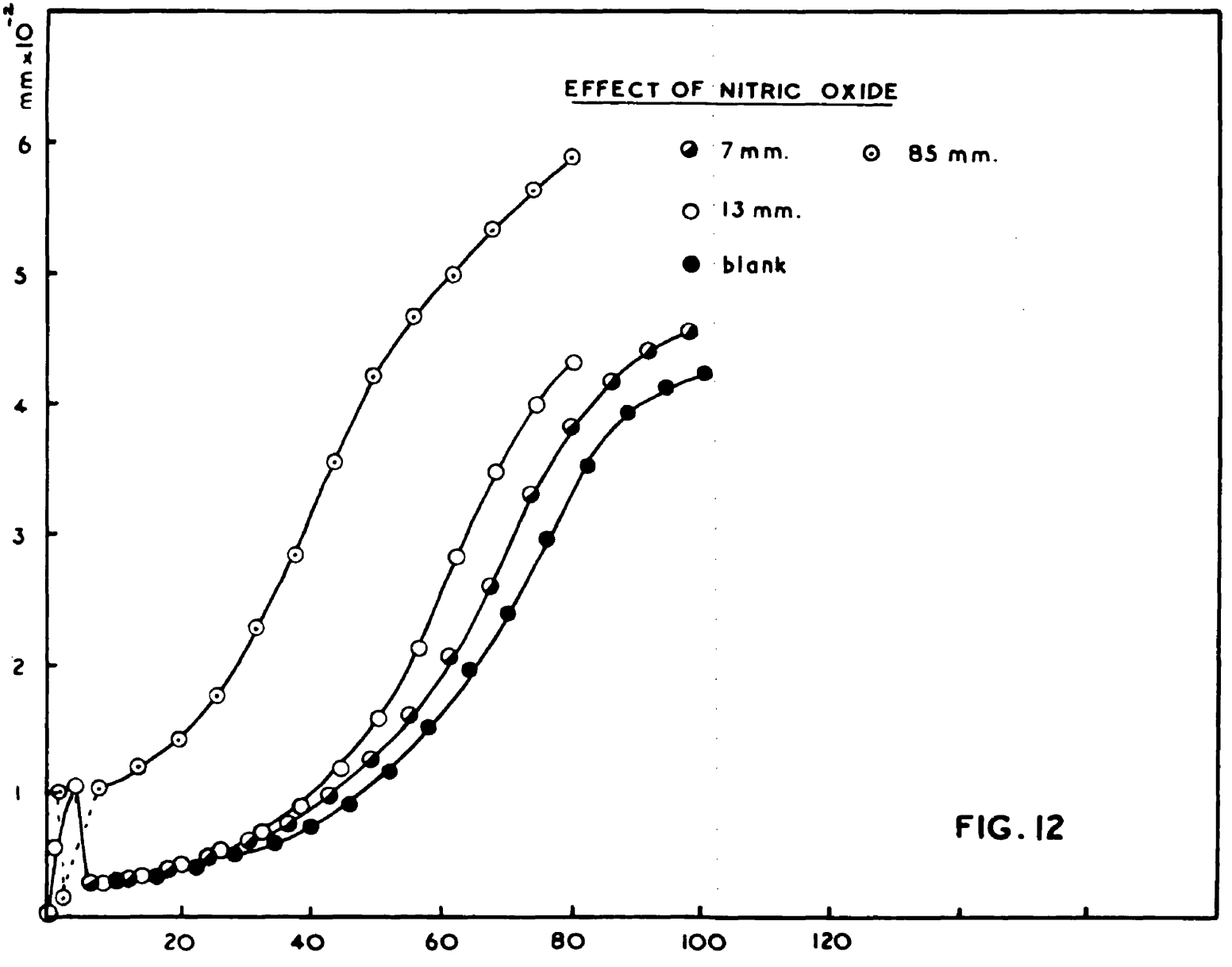

EFFECT OF NITRIC OXIDE
7 mm.
85 mm.
13 mm.
blank
mm x 10⁻²
6
5
4
3
2
1
20
40
60
80
100
120

FIG. 12

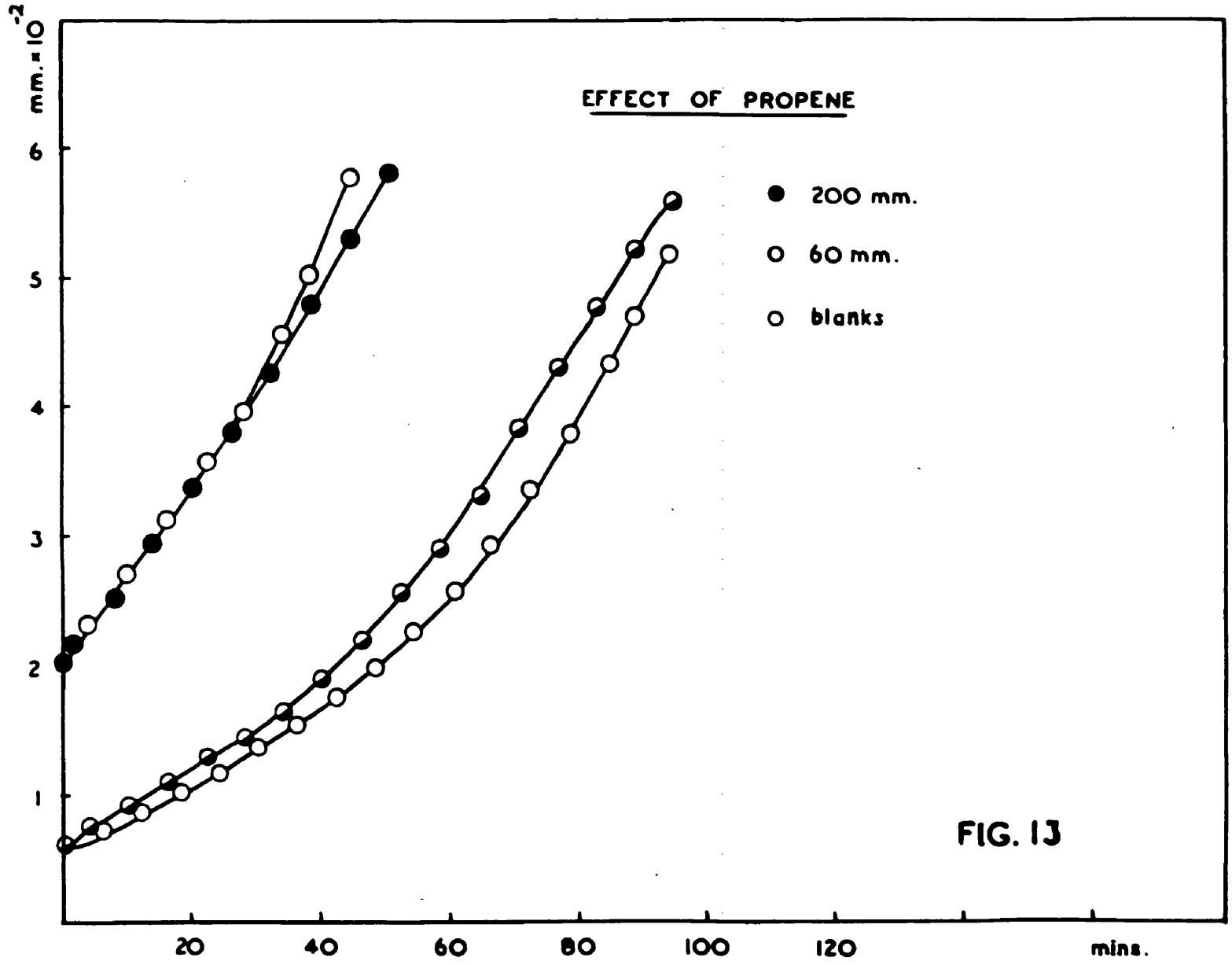

EFFECT OF PROPENE
mm. x 10^-2
6
5
4
3
2
1
20
40
60
80
100
120
mins.
200 mm.
60 mm.
blanks

FIG. 13

The effect of nitric oxide is shown in Fig. 12. Runs carried out in the presence of 3 mm., 7 mm., and 13 mm. nitric oxide gas indicated no change in the reaction rate. The maximum rate reached in every case was 11 mm./min., identical to that of the corresponding blank run, the times taken to attain these maxima also being the same. The initial pressure rise was not affected. Pyrolysis in the presence of 85 mm. nitric oxide gave the same maximum rate value, 11 mm./min., as in the other nitric oxide runs, but this rate was reached in 40 minutes, as against 60 minutes in the other pyrolyses.

The effect of propene was examined by pyrolysing vinyl benzoate in the presence of 60 mm. and 200 mm. of the gas (Fig. 13). Comparison to blank runs with corresponding pressures of nitrogen being employed indicated no changes in the reaction rates on adding the hydrocarbon gas. Vinyl benzoate free of ethylidene diacetate was used for these runs.

4.3.9. <u>The action of iodine.</u>

Figs. 14, 15, and 16 indicate the plots obtained on adding iodine to the vinyl benzoate pyrolysand.

In the first case (Fig. 14) the pyrolyses were carried out in a carbonised reactor. The presence of 1% iodine in the pyrolysand gave a rate maximum

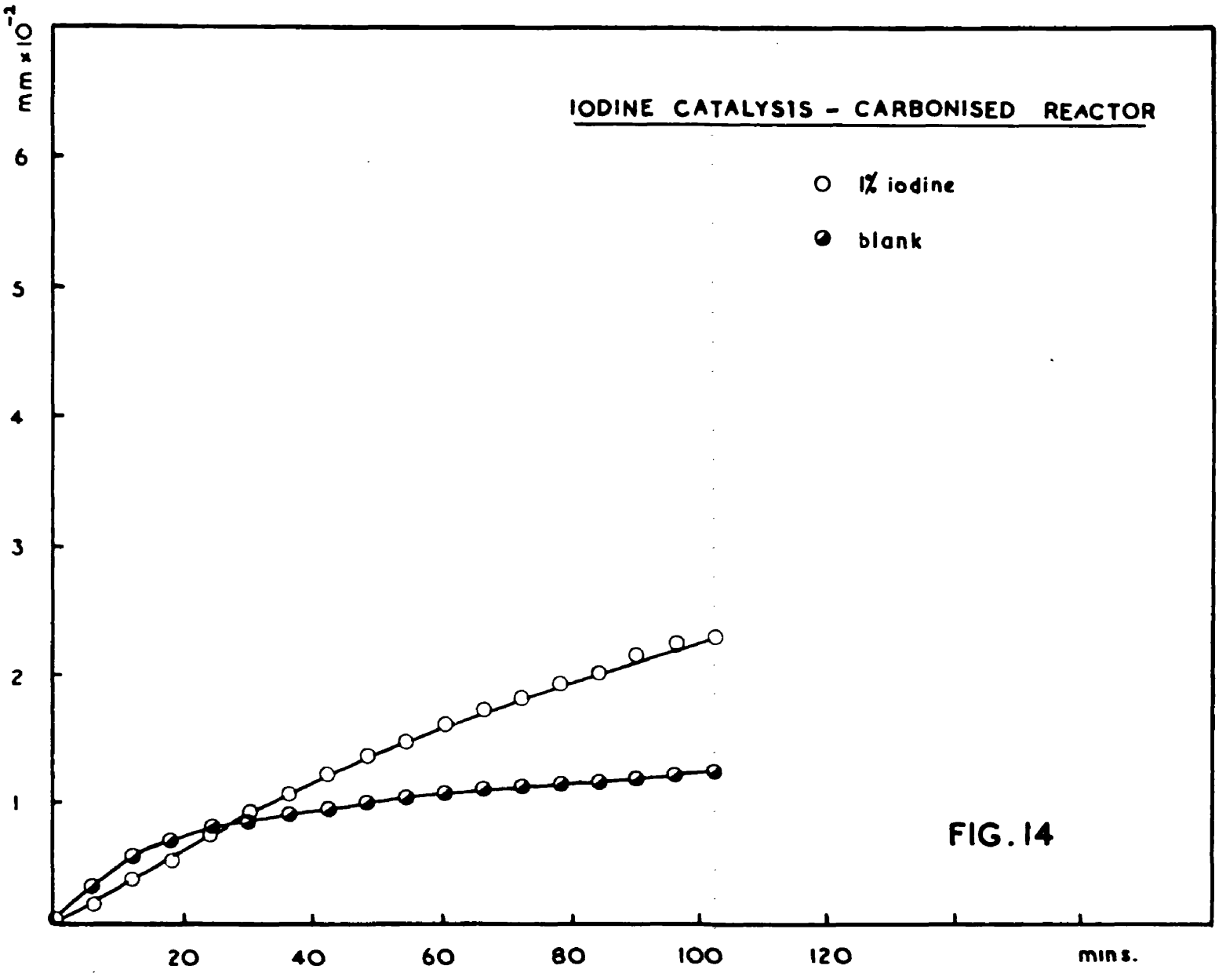

mm x 10⁻²
IODINE CATALYSIS - CARBONISED REACTOR
1% iodine
blank
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 14

of 2 mm./min., (the reaction being halted after 100 minutes), that of the blank run being ca. 0.75 mm./min.

Figs. 15 and 16 show plots obtained from experiments in a clean reactor. In the runs shown in Fig. 15, the pressure was allowed to reach 120 mm. before being reduced to 20 mm., and the run continued. With 1% iodine present, the maximum rate value was 20 mm./min. (after 32 minutes). For the blank, the maximum rate was 10 mm./min. (after 88 minutes). In the runs shown in Fig. 16 the initial pressure was allowed to reach 270 mm. before being reduced to 30 mm. In the presence of 1% iodine, the maximum rate value reached was 15 mm./min. (after 76 minutes). The corresponding blank run gave a maximum rate value of 5 mm./min. at 105 minutes, the run being stopped at this point.

The effect of iodine on the rate of pyrolysis of acetophenone was also investigated (Fig. 17). Using a charge of 2 ml. pyrolysand, acetophenone itself was found to degrade at an almost immeasurably slow rate, a pressure drop of 2 mm. in 40 minutes being recorded. The effect of adding 1% iodine to the ketone is shown in Fig. 17, when a curve with similar general characteristics to that of vinyl benzoate was plotted, with a maximum rate value of ca. 23 mm./min.

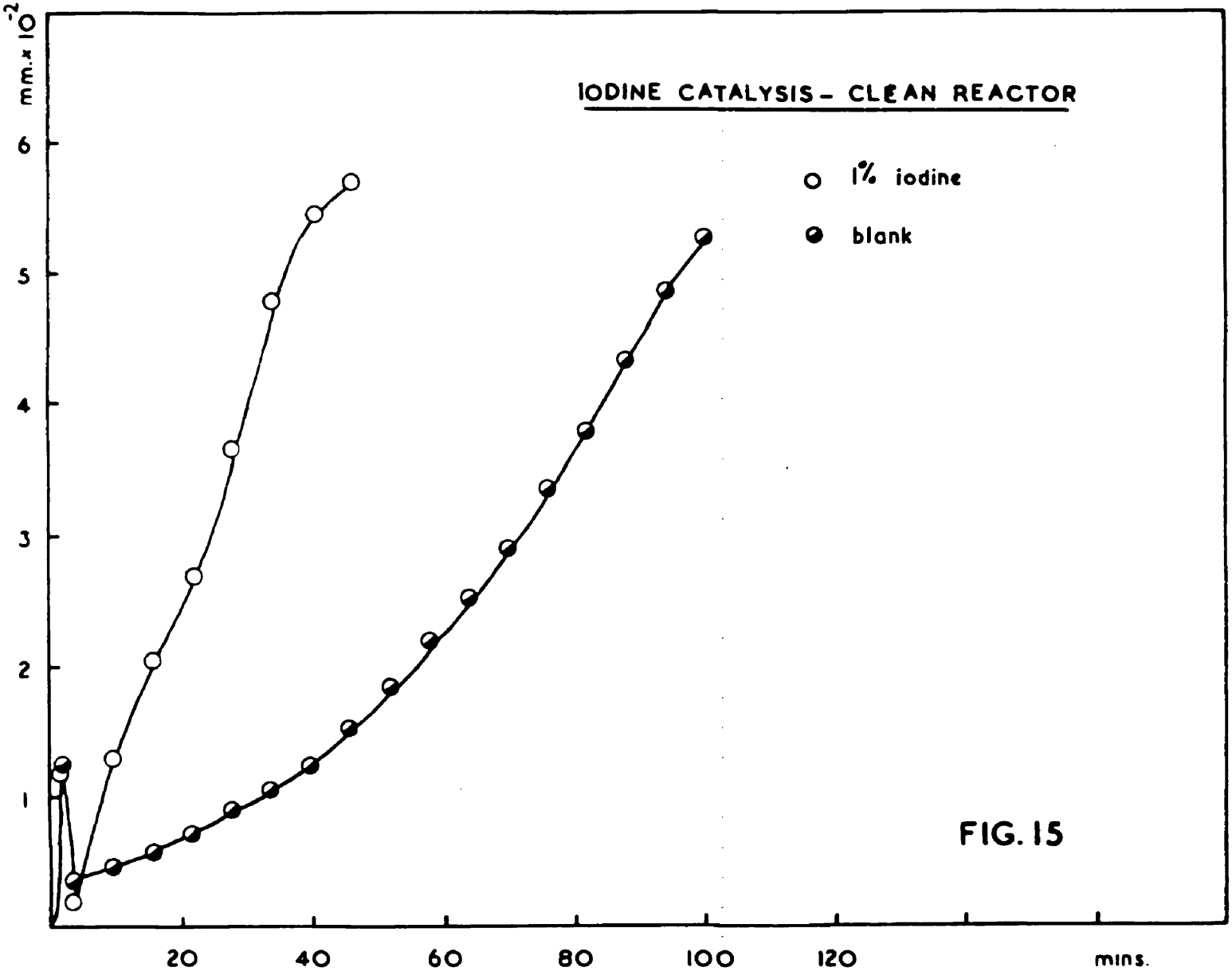

IODINE CATALYSIS - CLEAN REACTOR
1% iodine
blank
mm. x 10^-2
1
2
3
4
5
6
20
40
60
80
100
120
mins.

FIG. 15

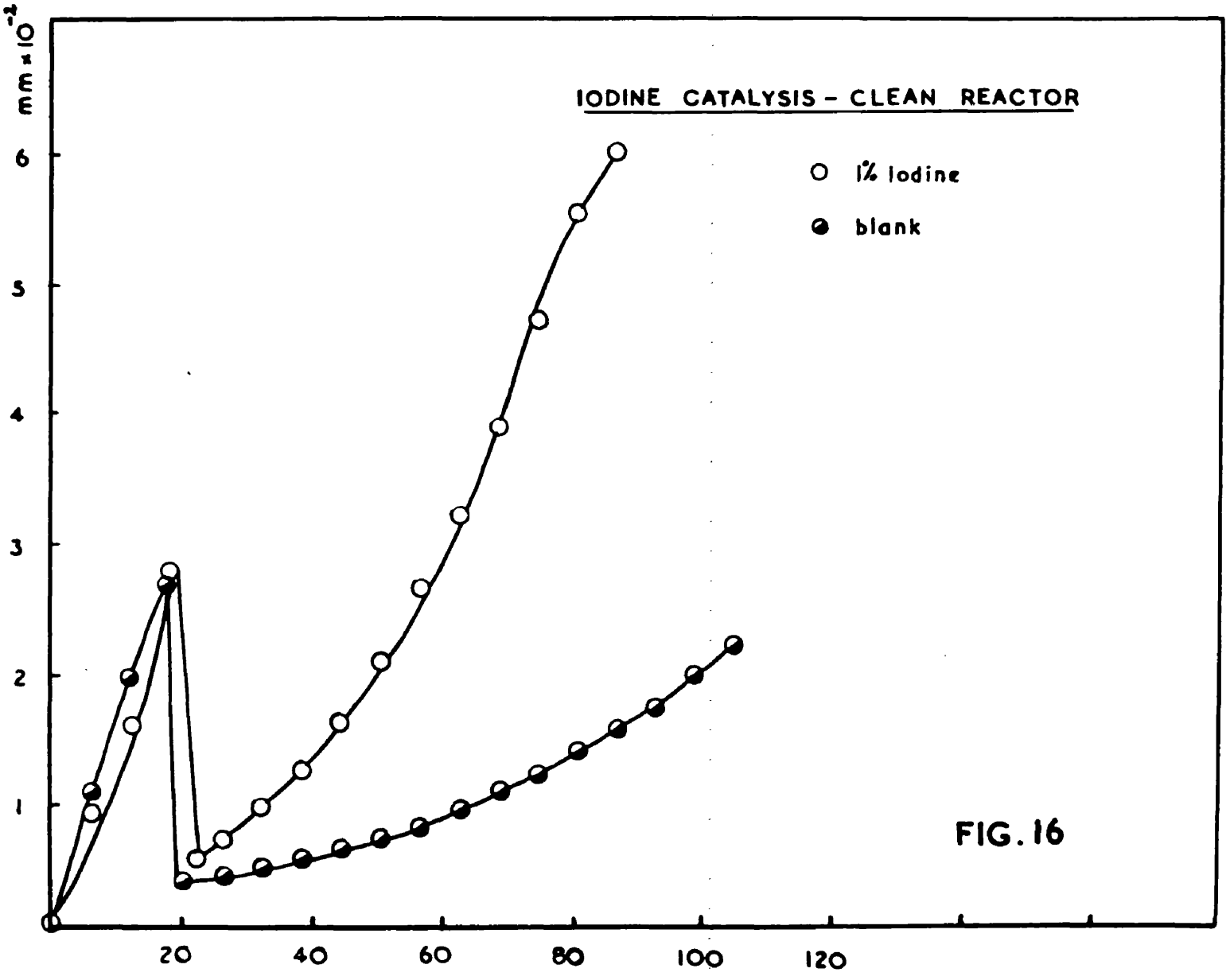

IODINE CATALYSIS - CLEAN REACTOR
1% Iodine
blank
EE x 10^-2
1
2
3
4
5
6
20
40
60
80
100
120

FIG. 16

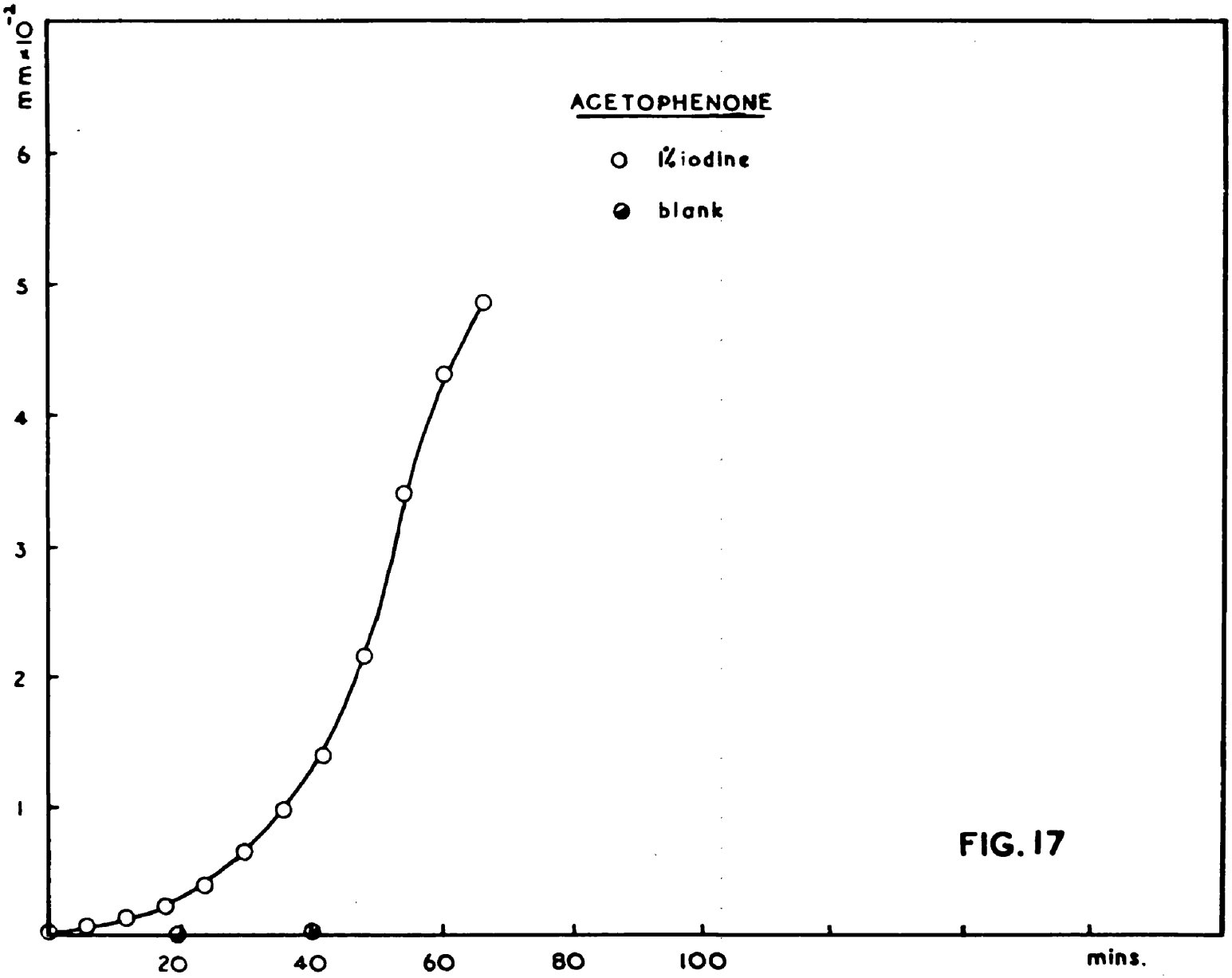

ACETOPHENONE
1% iodine
blank
mM x10⁻²
6
5
4
3
2
1
20
40
60
80
100
mins.

FIG. 17

In the course of the pyrolysis of vinyl benzoate in the presence of iodine, it was observed that, at the end of a run, carbonisation in the reactor tube was very heavy. Similar, but much less marked, effects were also recorded in those runs involving acetophenone and iodine. A pyrolysis of vinyl benzoate containing 5% carbon tetrachloride, while not giving any changes in the rate of the reaction, was also found to yield heavier carbonaceous deposits than normal, although again the effect was much less marked than in the case of iodine.

4.3.10. Packing effects.

Early runs in packed vessels were carried out by packing the full length of the reactor tube with glass wool. The observed rates were found to be dependant upon the distribution of the glass wool in the reactor. Fig. 18 shows plots for three runs in such a packed reactor. The rates obtained were ca. 1.5 mm./min. (at 60 minutes), 15 mm./min. (at 26 minutes), and 40 mm./min. (at 16 minutes), against a blank run of 12 mm./min. In no case in the packed reactors was there any visible reflux. In the first run, where the rate was very low, a slug of liquid was formed permanently at the top of the packing. The free volume of the reactor was measured by

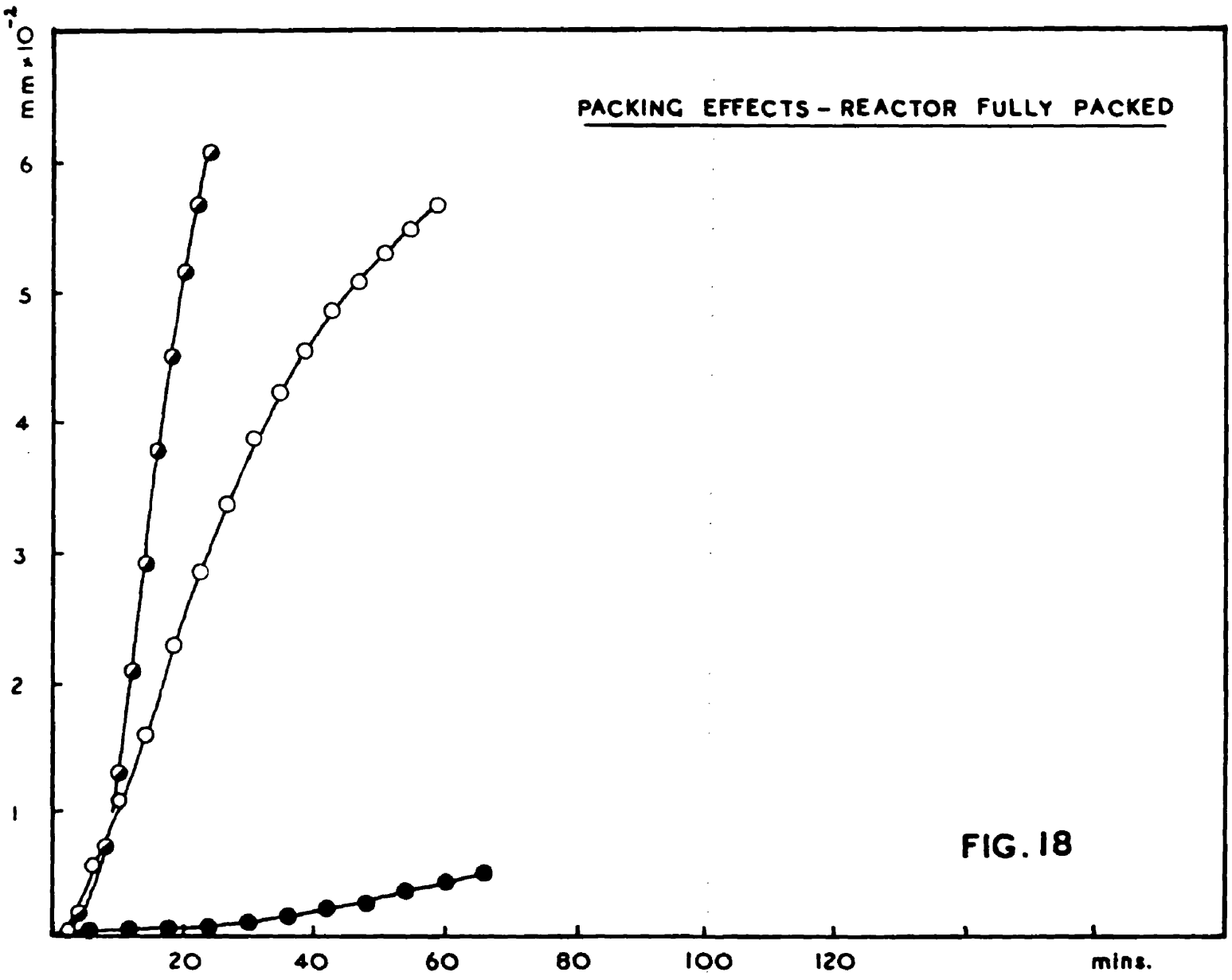

PACKING EFFECTS - REACTOR FULLY PACKED
E x 10^-2
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 18

"sharing" with a storage bulb of known volume, and was found to be 130 ml. in every case.

A run carried out in a reactor fully packed with rolled sections of "Fibreglass" diamond mat gave a rate maximum of 18 mm./min. As before, no reflux could be observed.

A number of runs were then carried out in a reactor packed with rolled sections of "Fibreglass" diamond mat, only the bottom 8 inches of the tube being packed. In these cases the ester refluxed in the air condenser as usual. The rate maxima for the runs shown in Fig. 19 were 15 mm./min., and 17 mm./min., the blank run giving a rate maximum of 12 mm./min. Successive runs carried out without cleaning the tube resulted, as before, in a steady lowering of the decomposition rate, and removal of the packing, which was impregnated with decomposition products, led to an immediate rate increase.

The reaction rate in packed or partially packed vessels was still found to be pressure-dependant. A noteworthy change, however, from the decomposition in an empty reactor was the elimination in most cases of the initial sharp pressure rise (see Figs. 18 and 19). When such a rise was observed in a packed reactor, it was in a small number of cases where

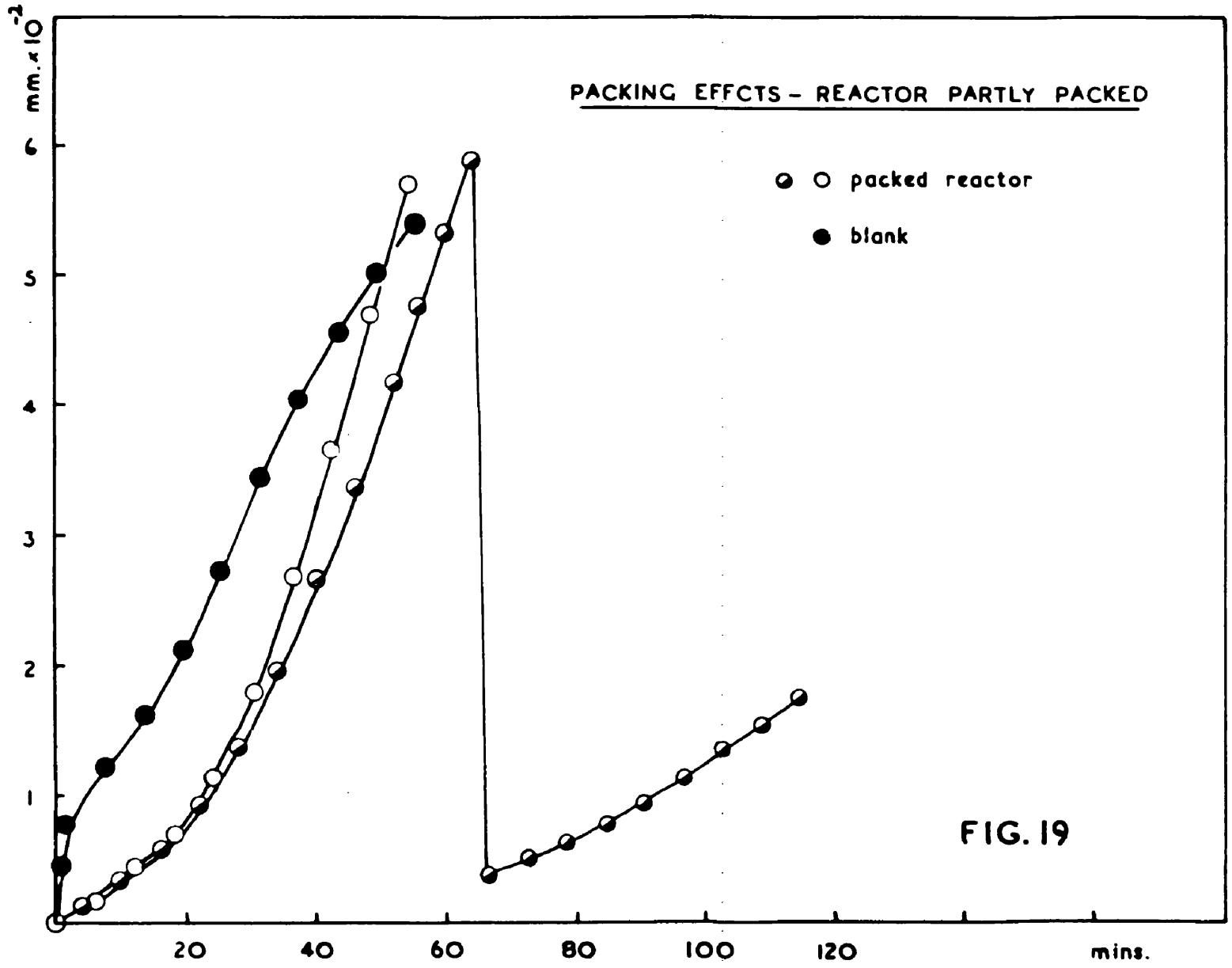

PACKING EFFCTS - REACTOR PARTLY PACKED
packed reactor
blank
mm. x 10^-2
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 19

packing extended over a shortened length of the reactor. Even in such cases, the initial pressure increase did not appear to take place with the normal rapidity.

Carbonisation in packed vessels, which was generally fairly heavy, was situated almost completely over the bottom 6 inches of the reactor.

4.3.11. Decomposition in blocked vessels.

In view of the rather ambiguous results obtained from packed vessels, the effect of partially blocking the reactor was examined.

It was found that, by placing two fairly tight glass wool plugs, each about an inch long, in each of the limbs, 2 inches below the bridge, the reaction could be almost completely stopped, the ester forming a slug of liquid on and above the glass wool.

A series of runs was carried out in a reactor having two glass wool plugs about 6 inches from the bottom of the reactor. The rate maxima were, within experimental error, the same as for the empty tube; thus, as shown in Fig. 20, the rate maxima in the blocked tubes were 15 mm./min. and 17 mm./min. However, in the first two cases, the maximum rate was reached in 26 minutes each time, compared with 48 minutes for the blank run. Moreover, on blocking the

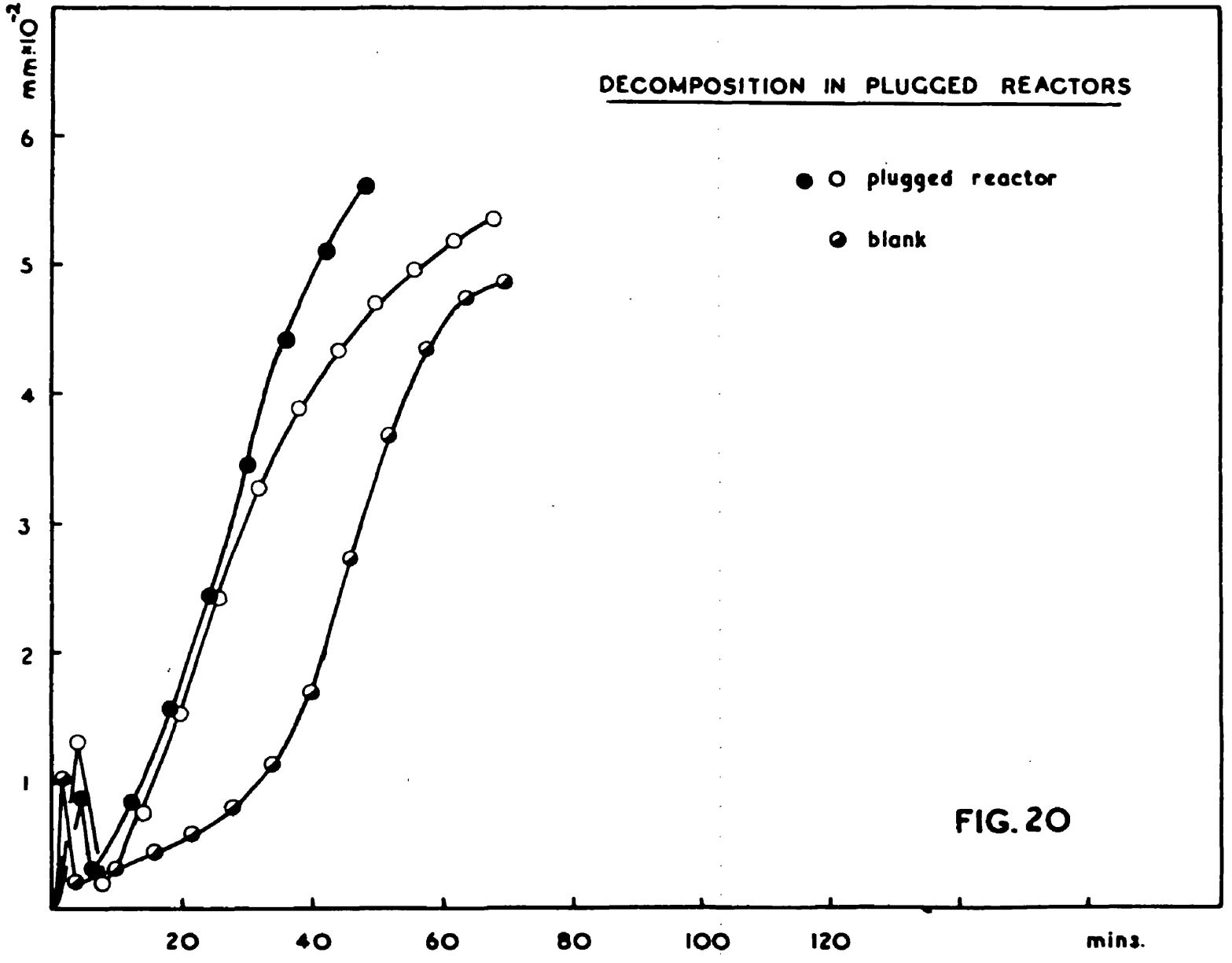

DECOMPOSITION IN PLUGGED REACTORS
● O plugged reactor
◐ blank
mm x10⁻²
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 20

reactor tubes, the quantity of liquid reflux was visibly reduced to a considerable extent.

4.3.12. Temperature changes

A pyrolysis carried out in an empty reactor at a temperature of 470°C gave an almost negligible cracking rate, apart from the initial rise. However it was found possible to induce greater degrees of decomposition either by packing the tube with glass wool, or by using two glass wool plugs, as described above, placed above the hot zone of the reactor. In both cases the quantity of refluxing liquid was considerably reduced. For the plugged tube, the measured rate maxima were 5 mm./min., at 470°C, and 17 mm/min. at 520°C; for the packed tube, the corresponding rates were 8 mm./min., and 40 mm./min.

4.3.13. Surface effects.

Pyrolyses were carried out in a test-tube reactor packed with copper turnings, and in a similar reactor whose walls were heavily coated with "silica" (Fig.21). No changes in the rates were found when compared to the blank runs. Similar rates were observed in a "Vitreosil" reactor of identical dimensions to the glass reactor.

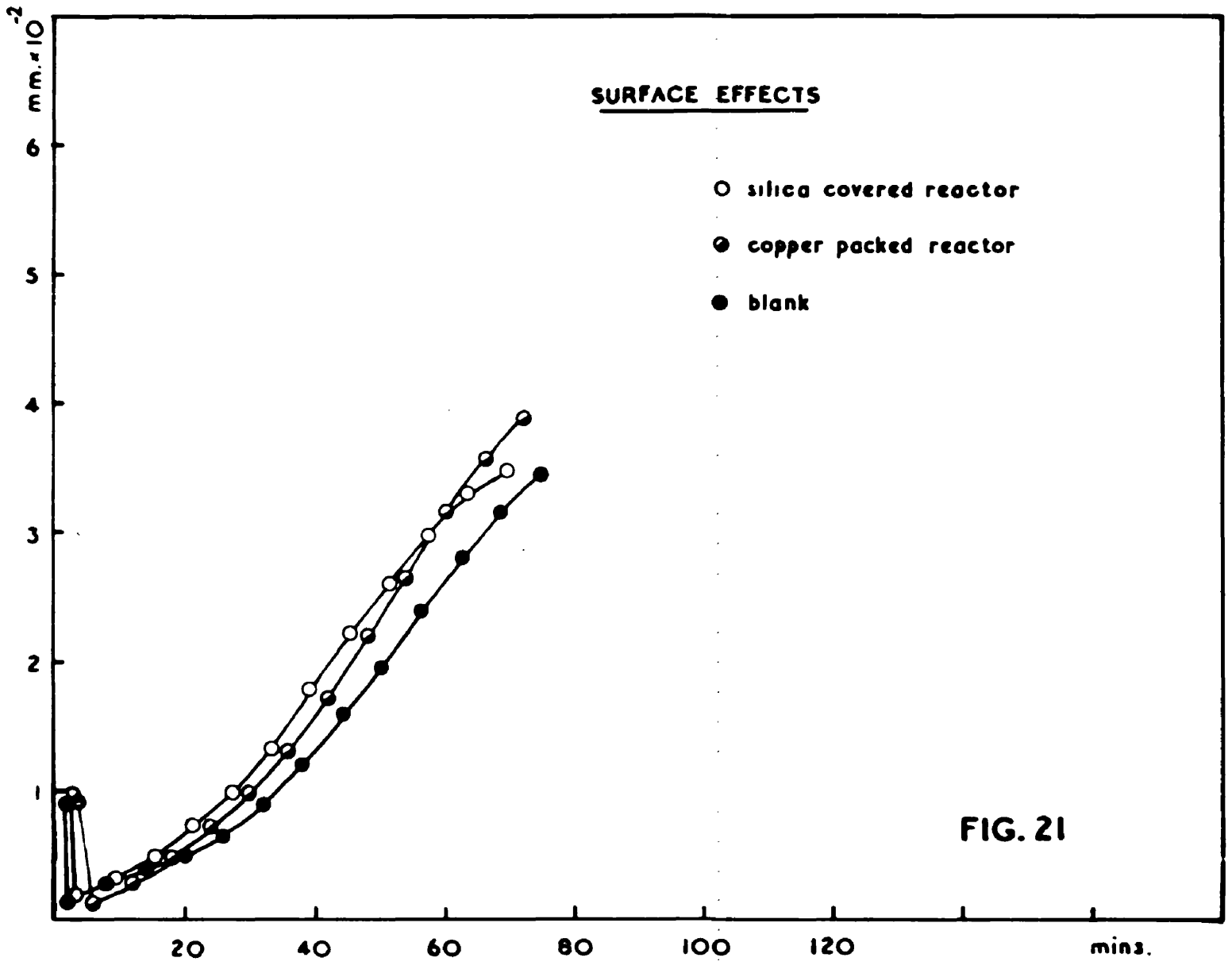

SURFACE EFFECTS
silica covered reactor
copper packed reactor
blank
mm. x 10^-2
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 21

A pyrolysis in a tube heavily carbonised by the decomposition of ethylidene diacetate likewise yielded a pressure-time curve almost identical to that given by the clean reactor.

4.3.14. Volume effects

The plots obtained from test-tube reactors of different volumes are shown in Fig.22. The curves shown were obtained from reactors of identical length, and varying diameters of 10 mm., 20 mm., and 35 mm. Each reaction was taken to 75 minutes, and the rate maxima recorded were: under 0.5 mm./min., (almost immeasurable), ca. 1.0 mm./min., and 8 mm./min., respectively. Comparing the total gas produced in 70 minutes, the figures were 28 mm., 90 mm., and 330 mm., respectively, and dividing by the square of the reactor diameter, these figures give comparitive gas volumes of 28 mm., 23 mm., and 28mm., respectively.

4.3.15. Alteration of still-head diameter.

Still-heads of different side-arm diameters (see Dia. 4) were employed in conjunction with a test-tube reactor of 20 mm., diameter. The still-head diameters were varied from 5 mm., to 20 mm., but no significant alterations in the reaction rates were detected.

The condensing system was also altered by

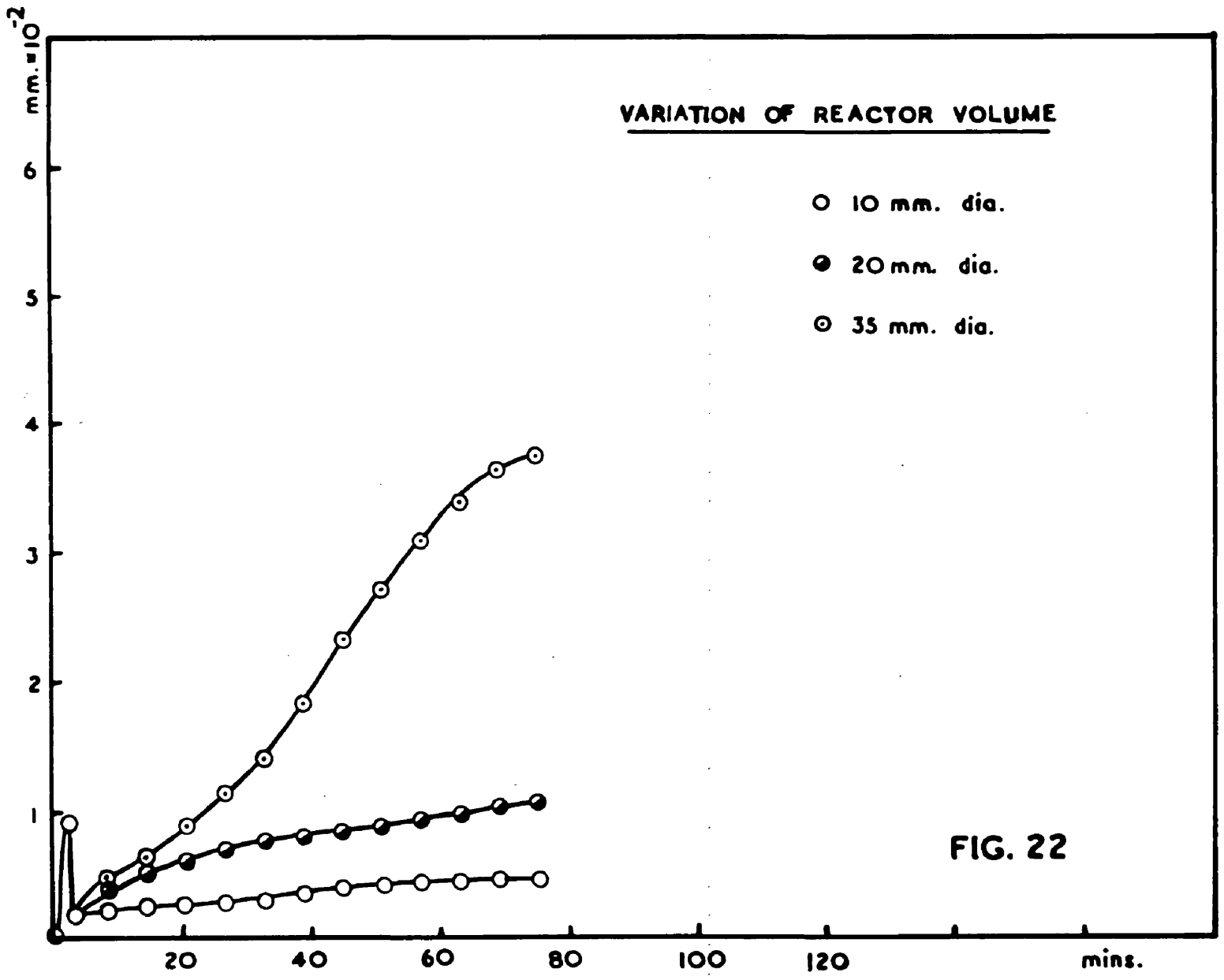

VARIATION OF REACTOR VOLUME
O 10 mm. dia.
20 mm. dia.
35 mm. dia.
mm. = 10^-2
1
2
3
4
5
6
20
40
60
80
100
120
mins.

FIG. 22

placing a water-condenser on top of the still-head. Similar rates were observed under varying conditions of water-flow. Efforts to lag the upper section of the reactor, the still-head, and the condenser, resulted in air-leaks occurring at the joint at the top of the reactor, and this system had to be abandoned.

4.3.16. Gas analysis

The results of gas analyses, and the conditions under which the corresponding pyrolyses were carried out, are detailed below.

RUN.	ANALYSIS					CONDITIONS
	CO_2	$CH{\equiv}CH$	C_nH_{2n}	CO	CO/CO_2	
1.	12.2	8.2	-	79.5	6.5	
2.	14.8	8.6	1.8	75.0	5.1	Dirty reactor
3.	14.4	3.1	-	82.5	5.7	
4.	18.1	1.9	0.1	79.0	4.4	
5.	16.1	4.6	2.8	76.5	4.8	
6.	12.7	8.2	3.0	76.1	6.0	
7.	15.1	7.3	2.9	74.7	5.0	
8.	14.4	6.9	2.4	76.3	5.3	
9.	15.2	4.5	3.7	76.6	5.0	60 mm. N_2 added
10.	15.9	4.3	3.0	76.8	4.8	200 mm. N_2 added
11.	19.8	-	-	80.2	4.1	180 mm. N_2 added
12.	18.4	-	-	81.6	4.4	Reaction taken to 60 mm.
13.	15.8	-	-	84.2	5.3	Reaction taken to 60 mm.
14.	13.8	5.5	2.3	78.4	5.7	Reaction taken to 200 mm
15.	14.2	8.3	3.8	73.7	5.1	5% Benzoic acid
16.	12.4	0.5	0.5	86.6	7.0	13 mm. nitric oxide
17.	11.8	8.5	3.2	76.5	6.5	14 mm. nitric oxide
18.	12.1	7.5	4.1	76.3	6.3	31 mm. nitric oxide
19.	13.5	-	13.8	72.7	5.4	83 mm. nitric oxide
20.	7.5	2.4	18.6	71.5	9.5	205 mm. propene
21.	15.2	4.9	13.7	66.2	4.4	60 mm. propene
22.	31.4	1.8	2.3	64.5	2.1	Glass wool packing
23.	16.0	2.8	2.0	79.2	5.0	475°C
24.	12.8	2.9	2.7	81.6	6.4	1% iodine
25.	17.4	1.3	3.5	77.8	4.5	1% iodine

The series of blank runs shown in the table (Nos. 1-8) were carried out at regular intervals in the course of the gas analyses. All of the pyrolyses detailed above took place in the static reactor, R.S.1., at a point when over 180 pyrolyses had been carried out in the reactor.

Saturated hydrocarbons were tested for in runs, 1, 2, 3, 15, 18, 22 and 25. Trace quantities were detected in runs 3, 22 and 25. The other runs yielded negative results.

4.4. The Pyrolysis of Esters Related to Vinyl Benzoate.

4.4.1. The pyrolysis of ethyl maleate.

A brief examination was made of the pressure-time relationships obtained by pyrolysing ethyl maleate in the static system, this ester being related to vinyl benzoate in that they are both high-boiling esters (vinyl benzoate, 203°C/760 mm. ; ethyl maleate, 225°C/760 mm.) of low volatility.

As indicated in Fig. 23, the rate of gas evolution from ethyl maleate at 520°C was found to be very slow, a rise of 10 mm. pressure being recorded in 33 minutes. Addition of 63 mm. nitrogen led to an immediate rate increase to ca. 1 mm./min. As the reaction proceeded, it

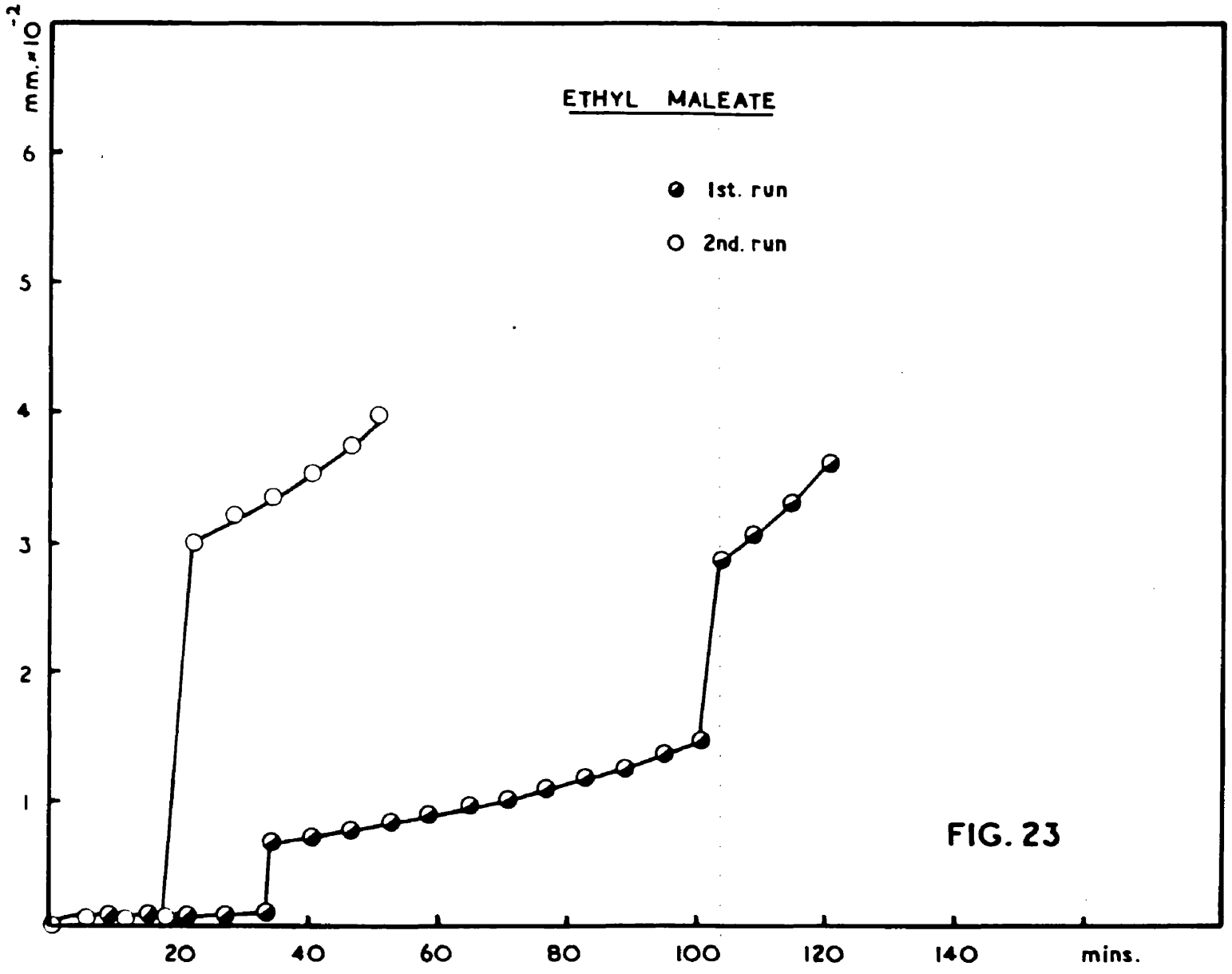

ETHYL MALEATE
1st. run
2nd. run
mm.x10^-2
6
5
4
3
2
1
20
40
60
80
100
120
140
mins.

FIG. 23

was evident that the rate was increasing with time, although this auto-catalytic effect was not as marked as for vinyl benzoate. Thus at 102 minutes, the rate had risen to ca. 2mm./min. Further addition of 157 mm. nitrogen at this point again caused a rate increase to a value of ca. 4.5 mm/min. In a second run addition of 290 mm. nitrogen caused a rate increase from a very low value to 2.5 mm./min.

4.4.2. The pyrolysis of ethylidene diacetate.

Ethylidene diacetate was pyrolysed in reactor R.S.1. Fig. 24 indicates the plots obtained from runs carried out at 490°C in packed and unpacked reactors. In an empty reactor, the pyrolysis of 1 ml. of the ester resulted in a very fast rise in pressure (204 mm. at 1 minute ; 240 mm. at 2 minutes). The rate then decreased very sharply, and quickly steadied down to a value of less than 0.5 mm./min. In a reactor packed loosely over its full length with glass wool, a rate maximum of 7 mm./min. was attained after 8 minutes. This rate was maintained for 40 minutes, after which gas evolution gradually decreased, until at 100 minutes the rate was 3 mm/min. At 100 minutes, the total pressure in the system was 511 mm., compared to 290 mm. at 100 minutes in the empty reactor.

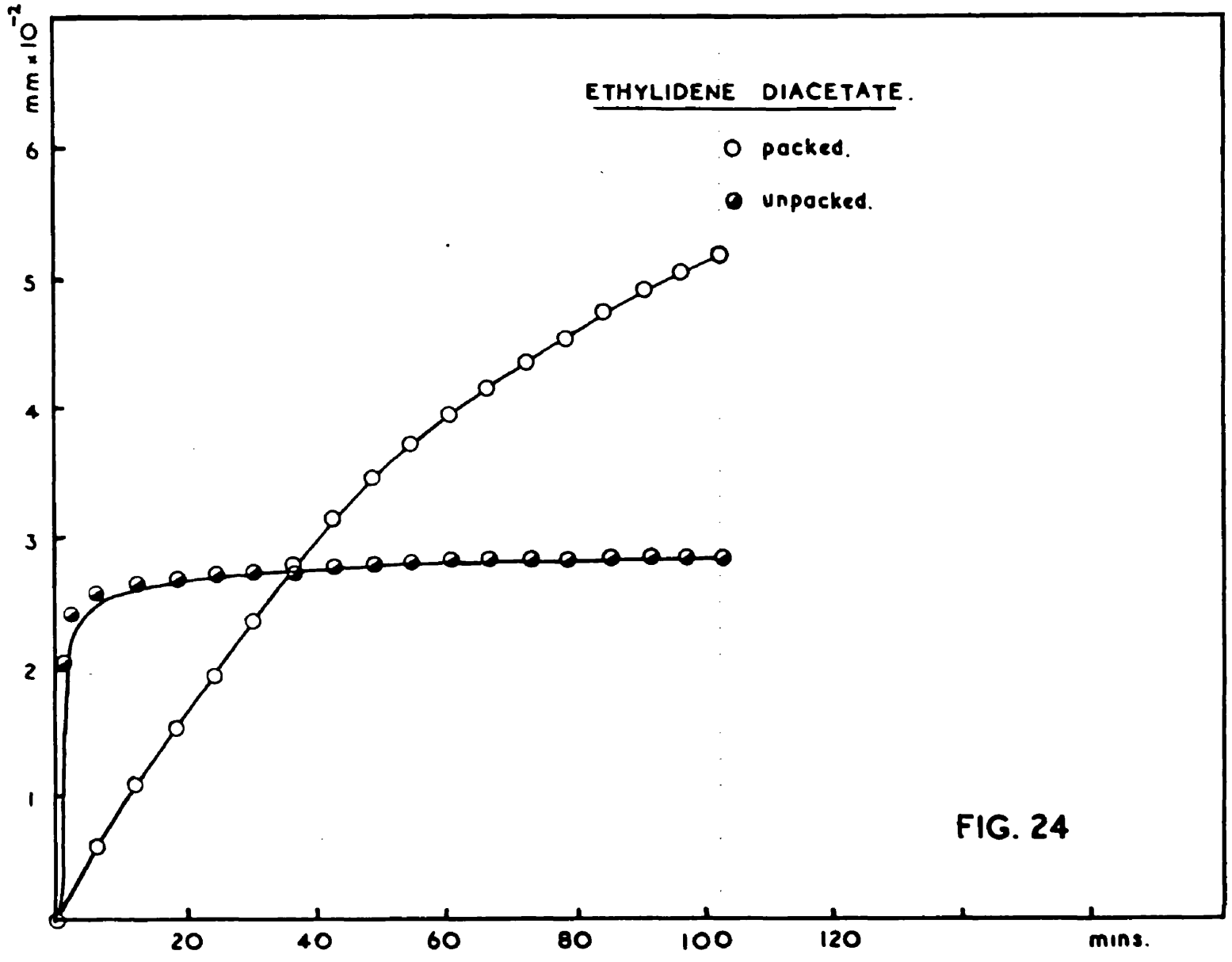

ETHYLIDENE DIACETATE.
packed.
unpacked.
mm x 10⁻²
6
5
4
3
2
1
20
40
60
80
100
120
mins.

FIG. 24

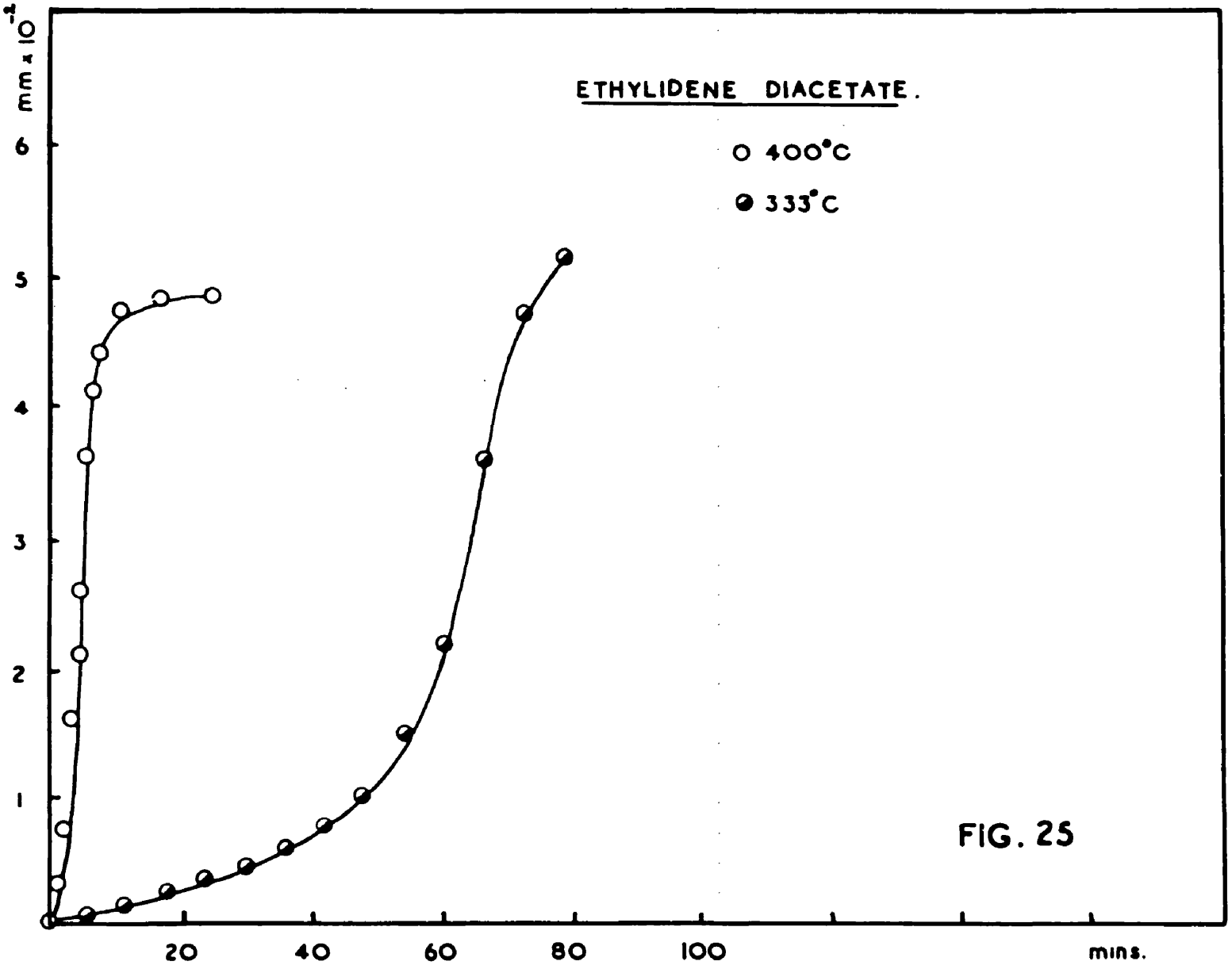

ETHYLIDENE DIACETATE.
O 400°C
● 333°C
EE x 10⁻⁴
6
5
4
3
2
1
20
40
60
80
100
mins.

FIG. 25

Runs carried out in both empty and packed reactors in the presence of 5 mm. nitric oxide indicated that the presence of the foreign gas did not alter the degradation rates within experimental error.

Pressure-time plots for ethylidene diacetate at lower temperatures were also obtained (Fig.25). While at 303°C, no pressure changes were observed after 20 minutes heating, the ester readily degraded at 333°C, to give a rate maximum of 27 mm./min. after 64 minutes. At 403°C, a rate maximum of ca. 100 mm./min. was reached very rapidly, at between 4 and 5 minutes, after which the rate decreased very rapidly to a value of less than 0.5 mm./min. In these runs at lower temperatures, 2 ml. ester were pyrolysed.

4.4.3. <u>The pyrolysis of vinyl acetate</u>.

A series of pressure-time plots for vinyl acetate is shown in Fig. 26 for temperatures varying from 625°C to 920°C. At temperatures below 550°C, the ester decomposed at an immeasurably slow rate. The pyrolyses were carried out in the "Vitreosil" test-tube reactor, the vessel previously having been carbonised by several pyrolyses of the ester, the reaction products subsequently being

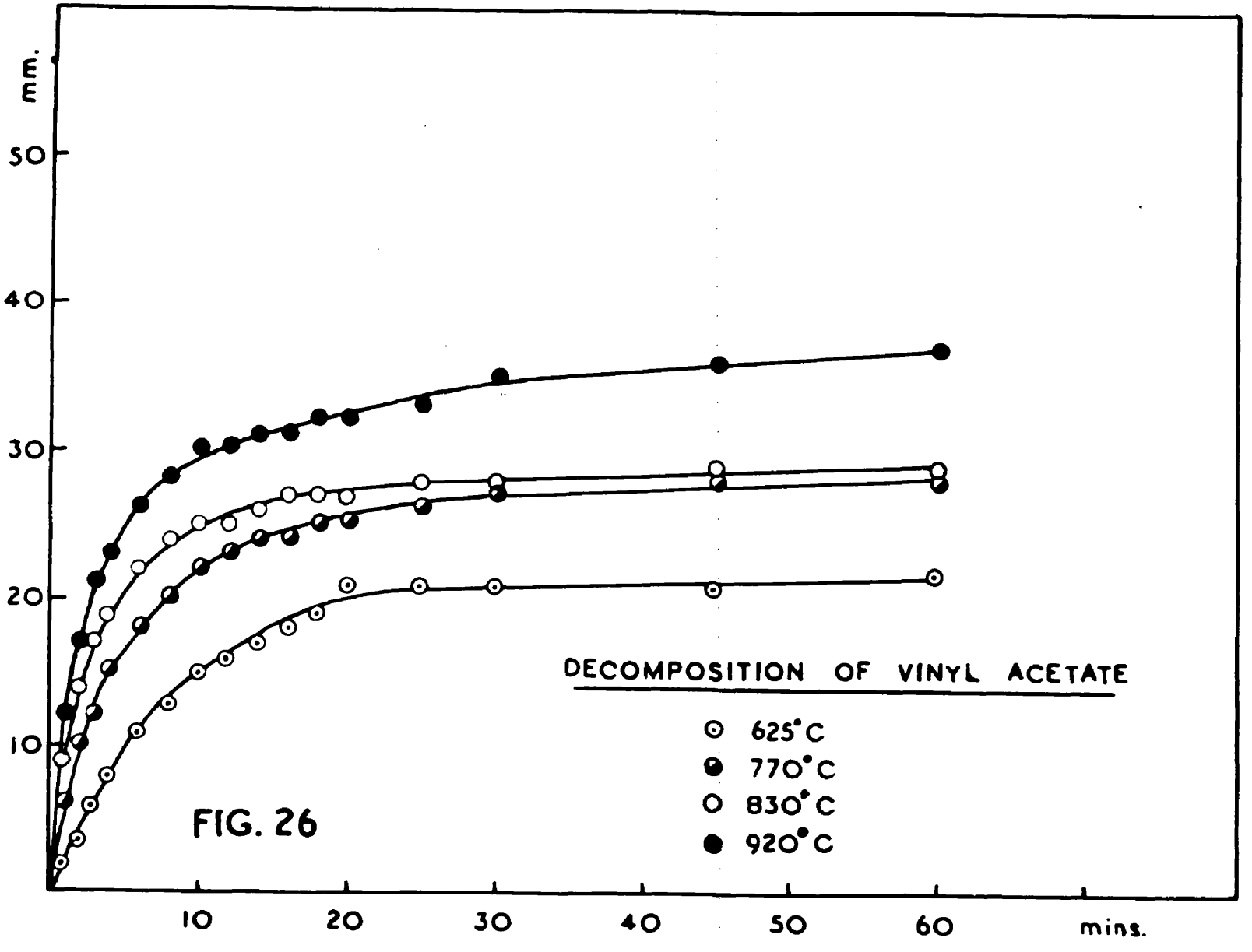

M.M.
50
40
30
20
10
DECOMPOSITION OF VINYL ACETATE
625°C
770°C
830°C
920°C
10
20
30
40
50
60
mins.

FIG. 26

pumped off. In the course of "seasoning" the vessel, no change in the reaction rate was observed, and later decarbonisation of the vessel again caused no change in the rate. A comparison of the pressure rise at various time intervals is shown below.

Time (minutes)	1.	2.	3.	60.	Temp.°C
Pressure (mm.)	12	17	21	38	920
	9	14	17	29	830
	6	9	12	28	770
	2	4	6	21	625

In the run at 920°C, the initial vinyl acetate pressure was 83 mm. In the other three cases, the vinyl acetate pressure was 74 mm.

The limits of reproducibility of these pyrolyses are indicated by the following results which show the pressure rise after 60 minutes in a number of runs carried out at 920°C :-

Pressure rise (mm.) :	35	37	38	42	35
Initial acetate conc. (mm.) :	86	87	83	86	77

The effect of foreign gases.

On pyrolysing mixtures of vinyl acetate and nitrogen in the proportions of one part ester to four parts nitrogen, the final pressure (i.e. the pressure at 60 minutes) was found to be appreciably higher than in corresponding blank runs using vinyl

acetate only (Fig. 27). Thus pyrolysis at 920°C of 70 mm. ester, using a total initial pressure of 346 mm. gave a pressure rise of 58 mm. after 60 minutes; pyrolysis of 60 mm. ester at the same temperature, using a total initial pressure of 293 mm, gave a pressure rise of 48 mm. after 60 minutes. In the corresponding blank run, an initial ester concentration of 82 mm. gave a pressure rise of 38 mm. after 60 minutes.

Similar effects were observed at 830°C. 60 mm. ester vapour in 283 mm. mixture gave a pressure rise of 44 mm. The corresponding blank run, using an initial pressure of 74 mm., gave a rise of 29 mm.

The presence of 5 mm. and 9 mm. nitric oxide in runs carried out at 920°C did not affect the reaction rate (Fig. 28).

Efforts to inhibit the reaction by the addition of cyclohexene could not be followed due to the immediate decomposition of the hydrocarbon gas at the high temperatures employed.

The presence of iodine vapour did not appear to affect the reaction. However, examination of the reactor on cooling indicated that the iodine condensed out on the upper parts of the vessel, and it is doubtful if the iodine vapour concentration

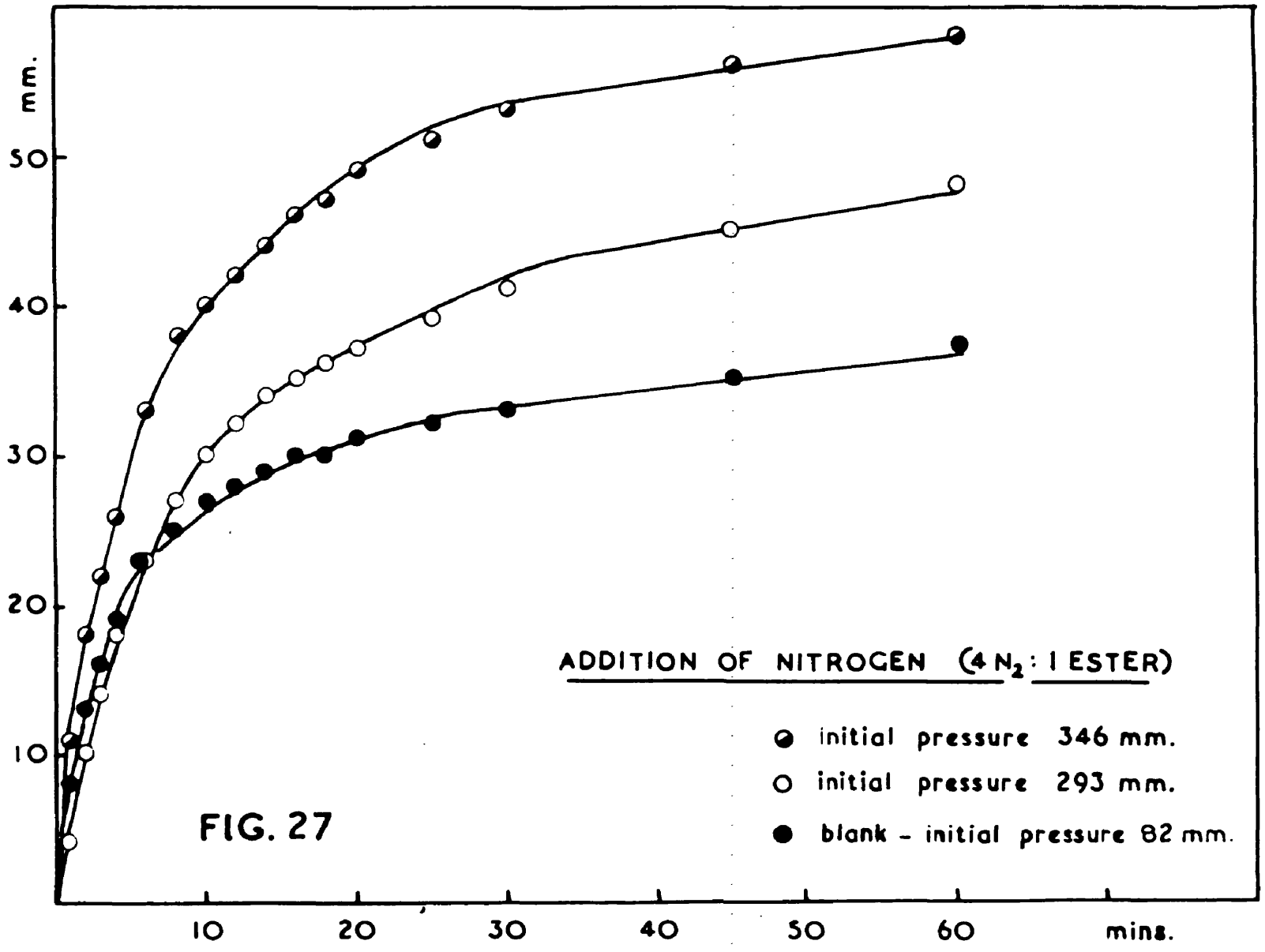

mm.
50
40
30
20
10
10
20
30
40
50
60
mins.
ADDITION OF NITROGEN (4 N2 : 1 ESTER)
initial pressure 346 mm.
initial pressure 293 mm.
blank - initial pressure 82 mm.

FIG. 27

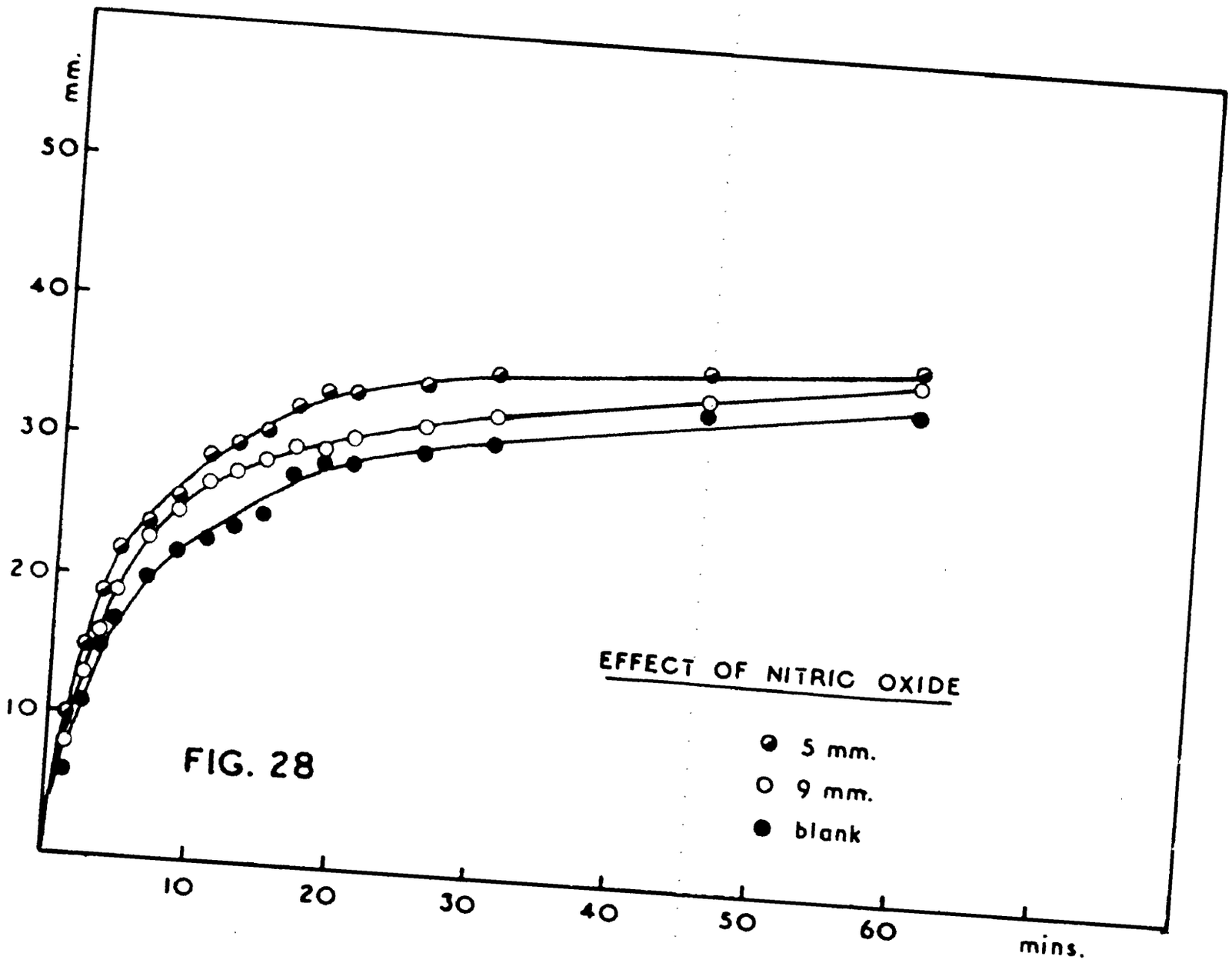

E.
E
50
40
30
20
10
EFFECT OF NITRIC OXIDE
5 mm.
9 mm.
blank
10
20
30
40
50
60
mins.

FIG. 28

was appreciable during the course of a run at the hot zone of the furnace.

Packing effects.

In a reactor partially packed with fine silica chips, such that the reactor volume was reduced from 145 ml. to 135 ml., while the available surface was greatly increased, rates similar to these of the empty vessel were obtained, within experimental error (Fig. 29). Thus, in a packed vessel, an initial ester concentration of 77 mm. gave a pressure rise at 60 minutes of 35 mm. In the blank run, an initial ester concentration of 86 mm. gave a rise at 60 minutes of 42 mm. These runs were carried out at 920°C.

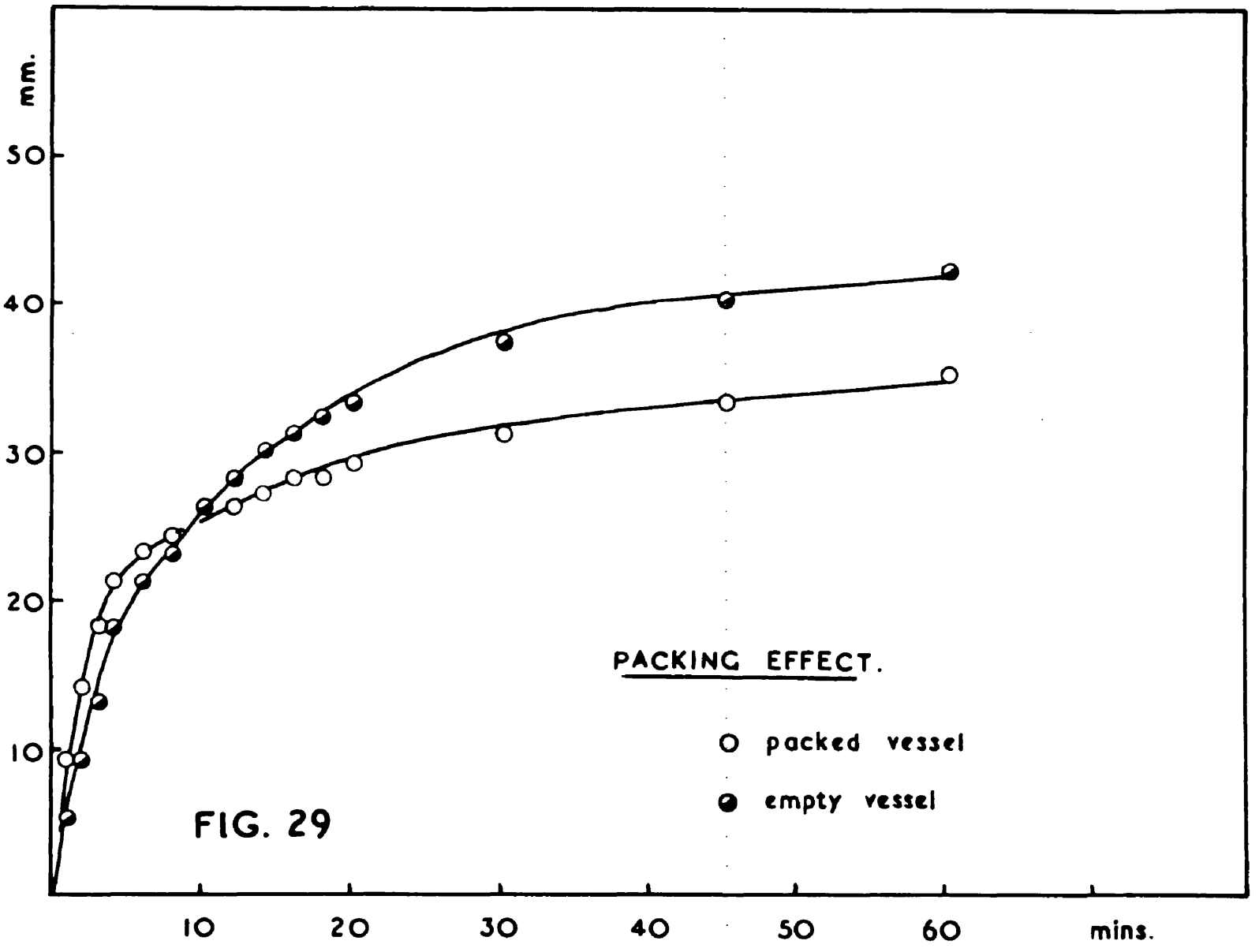

mm.
50
40
30
20
10
10
20
30
40
50
60
mins.
PACKING EFFECT.
packed vessel
empty vessel

FIG. 29

5. DISCUSSION.

5.1. The Pyrolysis of Vinyl Benzoate.

5.1.1. Limiting factors.

Any interpretation of the results of the investigation described in this work must be made in the light of certain limiting factors which were in operation continuously.

The difficulty of preparing pure vinyl benzoate was recognised by Allan, Forman, and Ritchie[10], who, by measuring the quantity of acetophenone produced at varying temperatures, estimated the threshold breakdown temperature as 190°C, i.e., just below the boiling point of the ester (203°C/760 mm.). It was evident, therefore, that high temperatures should be avoided if possible in any synthesis of the ester. While production of the ester from ethylene dibenzoate involved a pyrolysis in the region of 400°C, the highest temperature reached in the ester-interchange reaction was during the final distillation of the ester, normally carried out at 108°C/30 mm. An unforseen difficulty in the ester-interchange reaction was that of separating the vinyl benzoate from the ethylidene diacetate produced by the addition of vinyl acetate

to acetic acid. An attempt to separate the two esters by vapour-phase chromatography on a one-inch diameter column proved to be impractical (see Appendix). The final samples of vinyl benzoate, therefore, contained 5-10% ethylidene diacetate, and it was also found that the commercially available ester was, in fact, a similar mixture. It was decided, however, to use ester-interchange vinyl benzoate in the subsequent pyrolytic study, and this choice was supported by the following factors :

(i) The ester-interchange ester did not contain any degradation products of vinyl benzoate, one of which (benzoic acid) was shown to affect the reaction.

(ii) The ethylidene diacetate present decomposed rapidly in the reactor, and much of the acetaldehyde produced could be removed by reducing the pressure to ca. 10 mm. The other product of the decomposition, acetic anhydride, would not be expected to affect the following decomposition of vinyl benzoate, and the anhydride itself has been shown by Fischer, McLean, and Schnizer,[59] and by Brown,[60] to decompose to the extent of 20-30% at about 500°C, and under the present conditions it will be relatively stable.

(iii) The pressure-time curve of vinyl benzoate

"purified" in situ as described above was shown to correspond to that given by ester produced from ethylene dibenzoate. While both samples, therefore, contained impurities of different kind, they corresponded with respect to the measured rates. The ester-interchange ester, however could be more conveniently prepared in the laboratory, and, moreover, could be obtained commercially.

The limitation of the experimental techniques employed must also be taken into account. That temperature considered to be the 'temperature of pyrolysis' has been indicated as an arbitrary value, being the highest temperature in the furnace, and one which, in itself, could vary over as wide a range as 6°C. Three inter-dependant variables were also unknown with any degree of accuracy, viz., the effective volume of the reactor, the concentration of ester undergoing pyrolysis, and the contact time of the vapour in the reactor. It was evident from the area of deposition of carbon that degradation was occurring in the bottom 6 to 8 inches of the reactor, as would be expected from the temperature distribution in the furnace. This area covered a temperature range of 40°C. With regard to contact times in the hot

zone, these could not be estimated correctly, and indeed this value changed in the course of a run, as will be shown below. It is of interest to note that in a test-tube reactor of volume double that of reactor R.S.I., rates much lower than these of the normal static reactor were recorded. It seems likely that the bridge incorporated into the static reactor was allowing re-circulation of the hot vapours, causing a considerable increase in the contact time.

Hence it is evident that absolute kinetical data cannot be deduced from the recorded results, but a valid interpretation of these results can be made by reference to the control experiments which were carried out concurrently, provided that the boundaries of reproducibility of the reaction are clearly recognised.

The pressure-time curves could be closely reproduced over short time periods, both with respect to the general shape of the curve, and the maximum rate reached, but no just comparison could be made between runs separated by a period of months. In general, the seasoned reactor R.S.I. gave maximum rates at 520°C of between 10 and 20 mm./min. In any one series of runs, an

error of ±2 mm./min. was accepted. When differences of between 2 and 5 mm./min. between two runs were recorded, such changes were considered to be of questionable significance, and were not accepted unless such changes could be demonstrated to be consistent over four consecutive runs carried out in conjunction with corresponding blank runs.

A key to the reproducibility of the overall pyrolytic reaction is also afforded by the gas analyses, which are discussed below.

5.1.2. The overall reaction scheme.

While a quantitative analysis of the solid and liquid reaction products would have yielded the best means of following the reaction, such results could not be obtained with a satisfactory degree of accuracy because of the difficulty of analysing such a mixture of organic compounds, and of getting a homogeneous sample from the reaction tube. It was found, too, in some early investigations, that the gravimetric estimation of acetophenone (the main liquid product in the degradation) in vinyl benzoate samples was not satisfactorily reproducible (see Appendix). It was felt, therefore, that analysis of the gaseous products was the better means of following the reaction.

The primary routes in the pyrolysis of vinyl benzoate yield three gases, viz., carbon monoxide from route R/C[1], carbon dioxide from route C[2], and acetylene from route A[2]. In addition, small quantities of an olefinic hydrocarbon, identified by infra-red analysis as ethylene, have been found to appear consistently in the pyrolysate gases, the presence of which was also noted by Allan, Forman and Ritchie.[10] The origin of this gas is still obscure. Secondary decompositions will have little effect on the gas analysis. McKinnon and Ritchie[6] have found styrene to be stable up to 550°C. Acetophenone was found to be very stable in the static apparatus, except in the presence of iodine. Acetaldehyde arising from the decomposition of ethylidene diacetate will yield carbon monoxide and methane but the quantity of the aldehyde present was always negligible. Indeed, saturated hydrocarbons could not be readily detected in the gaseous pyrolysate. The decomposition of benzoic acid is of more significance to the gas analysis. Moser[61] found that, in glass, a heterogeneous decomposition reaction sets in at about 370°C. The major reaction is a decarboxylation to benzene and carbon dioxide, but a side reaction,

constituting 2-8% of the total breakdown, gives phenol and carbon monoxide, a reaction which, however, can be safely neglected. The decarboxylation reaction has no equilibrium point, and an acid concentration of 0.164 moles/litre was reported to have a half-life of 4.75 hrs. While it is difficult to estimate the contribution this reaction will make to the carbon dioxide figure in the gas analysis, a clue is given by Moser's observation that the reaction rate is increased 9-fold in the presence of copper. In the present work, pyrolysis over copper turnings did not result in any significant rate changes (Fig. 21). Moreover, it is evident from the acetylene analysis that 8% or less benzoic acid is produced by the primary route $A_2^?$ and in a series of runs, the acid can be seen to accumulate in the reaction tube. It seems likely, therefore, that decomposition of the acid under these present experimental conditions will little alter the gas analyses.

Examination of the gas analyses for the group of blank runs is a second indication of the reproducibility of the reaction under the conditions employed. The main route, R/C^1, varied in the approximate range 74-83% of the total reaction, and

a good average figure would seem to be about 76.5% of the total. Similarly, route C^2, indicated by the carbon dioxide figures, varied in the range 12-18%, and a good average figure would be 14.5% of the total. In the same way, by averaging the acetylene and ethylene analyses, a "typical" pyrolysis gas would yield :-

carbon monoxide	-	76.5%
carbon dioxide	-	14.5%
acetylene	-	6.0%
ethylene	-	3.0%

A useful comparison may be made by taking the ratio of carbon monoxide to carbon dioxide. Again, while this ratio has been found, in the blank runs, to vary from about 4.5 to 6.5, a good average ratio for the routes R/C^1 to C^2 is 5.2. These average figures are of value, but the range over which any one analysis can vary must be borne in mind. The method of gas analysis used (absorption analysis using a Sleigh gas analysis unit) will give errors in reading of not greater than 1%, and the variations in the analyses, which are particularly evident in the acetylene figures, must be presumed to be due to changes in the reaction conditions.

Generally gas samples were taken towards the end

of a pyrolysis, at the stage when the rate was slowing down rapidly. In three cases, however, gas samples were taken at earlier stages of the reaction (Analyses No. 12, 13, and 14), and the analyses indicate that the same overall reaction was being followed in the course of a pyrolysis, the CO/CO_2 ratios being 4.4 (at 60 mm. pressure); 5.3 (at 60 mm. pressure); and 5.7 (at 200 mm. pressure). Acetylene and ethylene analyses are not recorded in runs 11, 12, and 13 because of the very small samples which were taken in these runs. The total volumes analysed were of the order of 0.8 ml., hence the failure to detect the unsaturated gases, which would be present in volumes of 0.04 ml., or less, is not surprising. The gas analysis at 200 mm. pressure is typical of the reaction, and adds strength to the belief that the same reaction scheme is taking place, both qualitatively and quantitatively, throughout a run.

The gas analysis from a pyrolysis at 475°C lies within the same band as those at the higher temperatures. Such a phenomenon suggests that the various modes of breakdown have activation energies of the same order, i.e. that the rate changes of the various routes with respect to temperature are

similar. While this is a formal possibility, it is more probable that the band through which the analytical data can vary is too wide to reveal any changes taking place because of a temperature drop of 45°C. The rate of degradation was very small at temperatures much below 475°C, and precluded the possibility of gas analysis at lower temperatures.

5.1.3. The auto-catalytic effect.

The pressure-time curves recorded in the static apparatus are dominated by their auto-catalytic nature. A possible explanation of this characteristic can be offered if radical-chain processes are playing a prominent part in the reaction. If this were the case termination of the radical chain at the wall of the vessel would be expected to occur, such a reaction being a widely-recognised phenomenon in radical chain reactions. In the particular case of 1:2-dichlorethane, Howlett[62] observed that below an optimum pressure of 20 mm. pyrolysand, lowered rates resulted, and he attributed this to failure of one of the steps in the chain process. When wall-termination of a radical chain can occur, higher pressures will decrease the diffusion rates of the free radicals to the walls of the vessel, thus giving an overall increase in the reaction rate. This auto-catalysis

of a reaction will occur as the inert gas pressure in a system increases, and a plot with those characteristics exhibited by vinyl benzoate will be recorded. However, such an explanation in the present case is discarded because of lack of evidence for free-radical processes playing any significant part in the reaction scheme, as will be indicated below.

Another possibility to account for the auto-catalysis of the reaction may be offered by considering the major primary route, R/C^1, which has been suggested as giving acetophenone via the re-arrangement product, benzoylacetaldehyde. If, in this consecutive reaction, production of the intermediate β-ketoaldehyde rose gradually to a steady concentration, then an overall reaction rate increasing with time would result. This postulate must be dismissed for two reasons; firstly, the β-ketoaldehyde must be considered to be a transient, or compartively short-lived, intermediate, as evidenced by the failure to detect it in any pyrolysate, even when pyrolysis was conducted under mild conditions; secondly, a consecutive reaction theory fails to account for the immediate rate increase which arises on the addition of an inert gas to the system.

Reed and Thornley have found the decomposition of sodium adipate in the liquid phase to be autocatalytic, and have attributed this to mild catalysis of the reaction by the carbon deposited in the course of the decomposition. In the present work, neither carbon deposits or the reaction products have been found to have any positive catalytic effect.

It is now thought that the autocatalysis of the vinyl benzoate decomposition is a characteristic of the apparatus, rather than of the ester itself, and that the rate-controlling factor in the reactor is the rate at which the molecules may diffuse out of the cracking zone, this diffusion rate also governing the rate of reflux in the upper part of the reactor and in the condenser arm. This hypothesis is strongly supported by several otherwise un-correlated observations :-

(i) Other possible explanations are discredited in the light of the available evidence, as is detailed above.

(ii) Plots similar to those of vinyl benzoate have been recorded for diethyl maleate, ethylidene diacetate, and acetophenone.

(iii) In plugged vessels, where the hot zone was "isolated" by means of a glass wool plug, the

pressure-time curves tended towards a linear relationship with the pressure effect being much less marked. This effect may be explained by the increased difficulty that the hot vapours would encounter in diffusing from the cracking zone through the glass wool plug. A similar situation would exist in packed vessels. Thus the anomalous results obtained from packed vessels, wherein the rate was partly dependant upon the way in which the vessel was packed, can now be understood. It is also of significance that in plugged, and some packed, vessels, the quantity of liquid reflux was visibly reduced.

(iv) Although the approximate volume of the reactor is only 65 ml., it has been found necessary to use an initial charge of 3 ml. ester to obtain maximum rates, while conversely, with a charge of 1 ml. ester, a very marked depression was noted in the pressure-time relationship. Such behaviour indicates that by the time contact times in the reactor are at a maximum, the ester concentration has been reduced below the minimum value required to give maximum decomposition rates.

It will be seen, then, that the postulated diffusion effect can conveniently explain these

various results. The effort to alter the resistance to diffusion by the use of still-heads of differing diameter did not give very clear-cut changes in the rates of degradation. However, this is perhaps not surprising, as the critical area in any diffusion process would be expected to be the area containing the hot vapour-phase ester, rather than the refluxing liquid, and those experiments using glass-wool plugs indicate that this, in fact, is the case.

The rejection of a free-radical chain theory must, by the nature of the investigation, rest upon negative evidence. Coope and Bryce[64], investigating the thermal decomposition of dimethyl sulphide, found the reaction to be autocatalytic, but they failed to inhibit the reaction either with nitric oxide, or by packing the vessel. Nevertheless, they tentatively suggested a free-radical chain mechanism ; as they were working solely in the vapour phase, using a unit of negligible dead volume, there is some justification for their conclusions. In the present case, with due consideration for all of the available data, the diffusion hypothesis set out above is much more acceptable.

5.1.4. <u>The absence of radical-chain processes</u>.

That free-radical chain mechanisms can play an

important part in the pyrolytic decomposition of organic compounds is widely recognised. The production of a free-radical in any system would be expected to require an activation energy of the order of 10-30 k.cal./mole. greater than that of a molecular reaction yielding the same end-products. However, the free-radical once produced, may initiate a chain process of great length, in which the regeneration of the radical requires a small activation energy, and thus the primary initiation reaction, which is likely to be rare compared to the number of molecules undergoing change by direct molecular rearrangement, may in fact lead to the decomposition of many more units than the molecular mechanism, and hence play an important, and perhaps a major part in a thermal decomposition. For example, the thermal decompositions of diethyl ether[65], acetone[66], and cyclopentyl bromide[67] provide examples of reactions in which chain processes play an important role, and many similar examples have been reported in literature.

While the occurrence of chain mechanisms in any particular pyrolytic reaction cannot be predicted with any degree of certainty, such reactions are always to be considered as distinctly possible.

Bilger and Hibbert[68] speculatively suggested that free-radicals take some part in all ester decompositions. In the case of the predominant reaction, R/C^1, in the pyrolysis of vinyl benzoate, a plausible chain mechanism may be formulated :-

Initiation : $Ph.CO.O.CH=CH_2 \longrightarrow Ph.CO- + -O.CH=CH_2$

Propagation : $Ph.CO.O.CH=CH_2 + Ph.CO-$

$$\longrightarrow Ph.CO.O.\underset{\displaystyle CH_2.CO.Ph}{\underset{|}{CH-}}$$

$$Ph.CO.CH_2.\underset{\displaystyle O.CO.Ph}{\underset{|}{CH-}} \longrightarrow \left[Ph.CO.\underset{\displaystyle Ph.CO.CH_3}{\overset{\downarrow}{CH_2}}.CHO\right] + Ph.CO- + CO + Ph.CO-$$

Experimental evidence, however, points to the conclusion that radical chain processes are not taking a significant part in the vinyl benzoate degradation. Such a conclusion is supported by the following evidence :-

(i) Noted free-radical initiators and inhibitors have not been found to affect the reaction rate. Benzoyl peroxide and azodicyclohexanecarbonitrile, recognised initiating reagents, were non-effective. Conversely, the reaction could not be inhibited by the various quinones, toluene, copper, or more particularly, the gaseous inhibitors, nitric oxide and propene. In addition, Howlett and Barton[69] have reported the use of small quantities of acetaldehyde as a free-radical

inhibitor, and it may be considered as fragmentary evidence that the pyrolysis of vinyl benzoate containing ethylidene diacetate, which in turn leads to the production of acetaldehyde in the system, yields rates similar to those of the ester free from this impurity.

(ii) In packed vessels, no surface termination effects were observed, a phenomenon often associated with chain reactions.

(iii) Previous investigations[10] of the pyrolysis of vinyl benzoate did not reveal the complexity of products which might be expected to arise from a chain sequence. For example, if the chain mechanism outlined above were taking place, the following reactions might also result :-

$$Ph.CO- \rightarrow Ph- + CO \quad (1)$$

$$Ph- + Ph.CO.O.CH=CH_2 \rightarrow Ph.H + Ph.CO.O.CH=CH- \quad (2)$$

$$Ph.CO.O.CH=CH- \rightarrow Ph.CO- + CH_2=C=O \quad (3)$$

$$Ph- + Ph- \rightarrow Ph.Ph \quad (4)$$

$$Ph- + Ph.CO.O.CH=CH- \rightarrow Ph.CO.O.CH=CH.Ph \quad (5)$$

Hence ketene and diphenyl could arise <u>via</u> the reactions suggested in equations (3) and (4). Such products were not found, the known reaction products being those which can be accounted for by either primary or secondary molecular reactions.

While the rate measurements, therefore, suggest an

absence of free-radical processes, the gas analyses from those runs carried out in the presence of nitric oxide and propene are of interest. A brief consideration of the structural formula of any ester indicates that decarboxylation of an ester involves the breaking of two chemical bonds. A free-radical process might well be involved in the decarboxylation reaction, although it is difficult to envisage a chain sequence which would satisfactorily account for the reaction. The gas analyses in the inhibited runs will be seen to give consistently higher CO/CO_2 ratios, in the range 5.4 to 9.5, as against the "normal" range of 4.5. to 6.5. One low result is reported (a CO/CO_2 ratio of 4.4 being obtained in the presence of 60 mm. propene). While these results can by no means be claimed as conclusive, they do suggest that, to some extent at least, free-radicals are involved in the decarboxylation of vinyl benzoate.

It is of interest to note that Bailey and Hale[23] found that the presence of azo and peroxide catalysts, and quinone inhibitors, did not affect the alkyl-oxygen scission of 1-methylcyclohexyl acetate, while similarly Gordon, Price, and Trotman-Dickenson[52] found the alkyl-oxygen scission of tert-butyl formate to be unaffected by the addition of cyclohexene, a

free-radical inhibitor. McKinnon and Ritchie[6], however, have reported that the intra-acyl scission of phenyl formate can be suppressed by the addition of 1% quinol, and a free-radical mechanism has been outlined. A number of other free-radical inhibitors were found to have no effect, or a reduced effect, on the reaction.

5.1.5. Homogeneity of the reaction.

As indicated in Section 5.1.3. the ambiguous results obtained in packed reactors can be understood in the light of the diffusion process taking place in the reactor. In a fully packed reactor, rates were observed which ranged from an almost negligible rate to one which was approximately four times greater than the rates in the empty reactor, and it is now evident that this diversity of results was due to the effect of the packing on the dispersion of the liquid and vapour in the reactor. On the one hand, partial blockage of the tube at the top of the reactor caused the formation of a slug of liquid ester, whence low rates were observed due to a greatly reduced concentration of vapourised ester in the hot zone of the reactor. Conversely, in those cases where high rates of gas evolution were obtained, blockage of the tube must have been occurring rather lower down in the

reactor. This in turn would lead to increased resistance to the diffusion of the vapourised ester from the hot zone of the reactor, resulting in higher contact times in the cracking zone, and thus higher rates. The results obtained in blocked vessels, when rate maxima similar to the blank runs were reached in shorter times, and the pressure-time relationships tended towards a linear plot, substantiate this interpretation of breakdown in packed vessels. No decisive conclusions, then, can be drawn from these runs regarding the site of the reaction; the manner in which the vessel was packed clearly controlled the ensuing rate, which could vary over a very wide range.

A just comparison may be made between packed and unpacked vessels in those runs where packing was restricted to the cracking zone (evidently, from the area of deposition of carbon, the bottom 6 to 8 inches of the reactor), and, moreover, where reflux took place as normal. In such cases, the rates in the partly-packed reactor tended to be rather higher than the rates in the empty reactor, the recorded rate maxima being 13, 15 and 18 mm./min., against a blank run of 12 mm./min. These increases, however, are not large in relation to the large increase in surface area and

very small decrease in reactor volume under which these runs were carried out. It is apparent, then, that in the main, the pyrolysis of vinyl benzoate is a truly homogeneous reaction taking place in the vapour phase. The gas analysis for a run carried out over glass wool packing leads to a rather more detailed result. It is seen that, under such conditions, the gas sample was found to contain 31.4% carbon dioxide as against the "average" figure of 14.5%, and the carbon monoxide/carbon dioxide ratio was reduced to 2.1, as against the "average" of 5.2. The rate increases observed in partly-packed tubes, then, may be attributed in the main to a heterogeneous decarboxylation reaction at the surface of the vessel and packing. Again, however, that a very large increase in surface area only led to an increase in the carbon dioxide figures of rather more than double the normal indicates that this route itself occurs mainly by a homogeneous process. In addition, the increase in the carbon dioxide figure will be partly contributed to by the secondary decomposition of benzoic acid, already referred to as a heterogeneous decomposition[61], although this contribution will be a small one.

Two other pieces of evidence suggest the site of

the decomposition as being in the gas phase. Firstly, no change in rates were observed in the presence of copper, silica coating, or carbon deposits from ethylidene diacetate. Such surface changes might well be expected to affect a heterogeneous reaction. Secondly, the total volume of gas evolved in the decomposition has been shown to be roughly proportional to the available volume in the reactor. The overall decomposition of vinyl benzoate, then, may be regarded as a homogeneous decomposition with regard to the major route R/C^1, and route A^2, and mainly homogeneous, but with some degree of heterogeneous decomposition, with regard to route C^2.

5.1.6. <u>The reaction in a dirty reactor</u>.

The importance of carbonaceous deposits in thermal degradation reactions is widely recognised. The current studies of Bailey and co-workers[15,16,17,18,19,23] and other schools[20,21,22], on the isomerisation of olefins in the presence or absence of carbon deposits has already been referred to in Section 1.1.1. A more generally observed phenomenon is that of a steady depression of the reaction rate with successive carbonisations. Thus the observed rate fall in the present case is, to an extent, characteristic of a wide variety of pyrolytic gas-phase reactions. In general, such reactions yield

reproducible results only after "seasoning" of the reactor has taken place, and the number of runs required to "season" a vessel appears to vary very greatly. For example, Choppin, Frediani, and Kirby[70] report that only two runs were required before reproducible rates for the decomposition of ethyl chloroformate were obtained, while in contrast Barton and Howlett[71] report that over one hundred runs were required in the case of 1:2-dichlorethane.

In the course of the pyrolysis of vinyl benzoate, a limiting rate was approached after about ten pyrolyses. However, the experimental conditions in this investigation differed extensively in two particular aspects compared with the type of pyrolysis reaction referred to in the above examples. Firstly, the carbon deposits were heavy because of the large quantity of ester being used; secondly, the reaction products could not be removed because of their low volatility, and the presence of one of them was found to affect the reaction, as is discussed below. The lowered rates in the pyrolysis of vinyl benzoate may be attributed to three factors :

(i) A seasoning effect in the vessel.

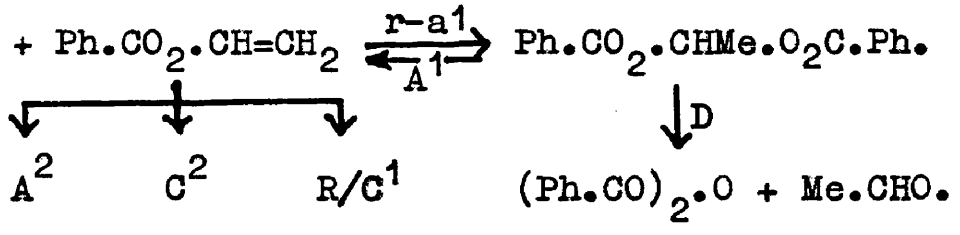
(ii) The presence of benzoic acid.

(iii) The presence of anti-catalytic carbonaceous deposits.

(i). Barton and Onyon[72], and Cullis and Priday[73],

have attributed the falling rates in seasoned vessels as being due to the elimination of heterogeneous decomposition at a clean glass surface, and it seems likely that this wide-spread phenomonen is occurring in the case of vinyl benzoate. This is suggested by the uniquely high rates which were obtained in the new glass reactor, and which could never again be attained, even after the most stringent cleaning processes. It would appear that the surface had been permanently affected in some way. Deposition of a heavy coat of silica on an already seasoned tube did not affect the reaction rate. The nature of these initial surface changes, then, is obscure. The main reaction in a "cleaned", seasoned tube is, as already outlined, predominately homogeneous.

(ii). The rate depression caused by the addition of benzoic acid is surprising, and occurs by a mechanism not yet understood. The co-pyrolysis of vinyl benzoate and benzoic acid is known to lead to the formation of ethylidene dibenzoate, which in turn undergoes a dis-proportionation to benzoic anhydride and acetaldehyde[5] :-



Allan, Jones and Ritchie[5] have found that, during the pyrolysis of the ethylidene diester at 500°C, routes D and A^1 occur as competitive routes, the former being the major route. While it seems likely, then, that reaction r-A^1 is the slow step accounting for the observed rate depression, (route D will occur relatively rapidly, the diester being less stable than vinyl benzoate), it is difficult to understand why the presence of as little as 5% acid can halve the maximum rate of gas evolution, while further additions of acid have no greater effect upon the rate.

(ii). The accumulation of benzoic acid in the pyrolysis tube in successive runs will account, in some degree, for the lowered rates but, on the basis of the co-pyrolysis experiments, cannot explain the very low rates eventually recorded. Apart from the benzoic acid, then, the deposited carbonaceous films would appear to exert an anti-catalytic effect upon the decomposition of vinyl benzoate. The role of carbonaceous deposits in pyrolytic degradations is not clear, as the conflicting results regarding double bond isomerisation[15-23] indicate. Carbon normally acts as a positive catalyst, or alternatively is used as a catalyst support in heterogeneous reactions.[74] It is therefore rather surprising to find, in the

present case, that the accumulation of carbon leads to a large rate depression. The rate depression appears to be associated with the deposition of carbon from the reaction being studied, as a carbon deposit from the pyrolysis of ethylidene diacetate did not affect the vinyl benzoate breakdown. It may be, therefore, that the carbon is not acting as a negative catalyst to the principal reaction, but rather as a positive catalyst to the competing reaction between vinyl benzoate and the accumulating benzoic acid. The impossibility of separating the two major solid phases in a dirty reactor, viz., benzoic acid and the carbonaceous deposits, without altering the physical nature of the latter, makes it difficult to assess completely the reaction in a carbonised tube, but certainly the presence of the carbonaceous deposits in some way cause a rate depression over and above that which can be induced by the addition of benzoic acid itself.

Retardation of a decomposition reaction due to the presence of reaction products is an established phenomenon in heterogeneous reactions, the rate depression being due to the reaction products being preferentially absorbed at the reaction sites at the surface. However, the vinyl benzoate reaction has

been shown to be homogeneous, and even if heterogeneous reaction were taking place at the carbon surfaces, the residual homogeneous reaction would maintain the normal rate, and, indeed, one would expect a rate increase in the overall reaction.

5.1.7. Pyrolysis in the presence of iodine.

Iodine is recognised to have a very marked catalytic effect upon the thermal decomposition of many organic compounds.[75] Bairstow and Hinshelwood concluded a series of investigations by noting that ethers and aldehydes in general were affected by iodine catalysis; some amines and esters studied also exhibited markedly increased decomposition rates in the presence of iodine. Methyl formate and methyl acetate were affected in this manner, the decomposition rates being increased by a factor of about 50 in the presence of 10 mm. iodine.[76] The decompositions of acetone and methyl ethyl ketone were reported to be unaffected by iodine, but later workers[77,78] found that the acetone reaction was accelerated.

Two facts emerge in the present work : the overall decomposition of vinyl benzoate is catalysed by the presence of iodine, and the decomposition of the major non-gaseous reaction product, acetophenone, is very strongly catalysed by the presence of iodine.

In the case of the ester, the rate maximum was increased by a factor of between 2 and 3 in both carbonised and uncarbonised tubes by the addition of 1% iodine. While in part this observed acceleration will be due to a catalysed secondary decomposition of acetophenone, the ester itself must be undergoing catalytic decomposition; the rate maxima for vinyl benzoate in the presence of iodine were 15 and 20 mm./min. (the difference being due to the initial pressure increases being taken to different stages), while the catalysed pyrolysis of 2 ml. acetophenone gave a rate maximum of 23 mm./min. The rates for the ester, therefore, are too high to be accounted for solely by the decomposition of the accumulating ketone. Moreover, the ester decomposition is accelerated immediately, before any acetophenone is present in the system. Nor could the acceleration be due to the presence of ethylidene diacetate, for in one run the initial pressure rise was allowed to reach 270 mm., sufficiently high to ensure the complete destruction of the diester, whose reaction products were then removed from the system. The trace of acetaldehyde remaining could not account for the high rates over a pressure range of 600 mm. observed thereafter. It is apparent, then, that the decomposition of vinyl benzoate itself is catalysed by

the presence of iodine, although the effect is not a particularly strong one.

The mechanism of the catalysed reaction cannot be defined in precise terms. The suggested intermediate compound in the major route R/C^1 is benzoylacetaldehyde, which might be expected to decompose catalytically under the influence of iodine in common with other aldehydes. Failure, however, to detect this β-ketoaldehyde in the course of pyrolysing vinyl benzoate strongly suggests that its existence is, in any case, very short lived. Again, if it were an accelerated decomposition of this intermediate that was being recorded, an increase in the carbon monoxide content of the pyrolysis gases would result, and that did not occur. This fact, in turn, suggests that it is the ester itself which is in some manner being activated, with subsequent decomposition by all three routes taking place.

Iodine catalysis in general is associated with the abstraction of a labile hydrogen atom, which can lead either to the formation of a free-radical which in turn initiates a chain decomposition, as has been suggested for acetone by McNesby, Davis, and Gordon,[78] or to a cycle of molecular reactions, as has been suggested for acetaldehyde by Hinshelwood, Clusius, and Hadman,[79] In the present case, a more acceptable explanation may

be offered in general terms. Bairstow and Hinshelwood commented on the difficulty of outlining a definite reaction sequence for the iodine catalysed decomposition of esters, and suggested that activation of the ester molecule was occurring by transfer of vibrational energy of the iodine molecule via a simple bimolecular collision, such collisions being encouraged by the dipole moment of the ester molecule in conjunction with the polarizable structure of iodine. This hypothesis was supported by the lowered activation energies in the catalysed decompositions of some ethers and aldehydes, such a decrease suggesting a change from a monomolecular reaction of high activation energy to a simple bimolecular reaction. Such an explanation seems very plausible to account for the catalysis of vinyl benzoate, for a distinct reaction sequence would be expected to lead to the catalysis of one route, rather than the generally catalysed reaction indicated by the unchanged gas analysis.

During the course of these catalysed pyrolyses, carbonisation was much heavier than usual, and it is interesting to note that Gantz and Walters[77] have also observed heavy carbon deposits in the iodine-catalysed decomposition of acetone. The catalysed decomposition of acetophenone also led to the deposition of fairly

heavy carbon films, but no comparison could be made to the uncatalysed reaction, which was exceedingly slow.
Wright[80] found that the co-pyrolysis of p-ethylacetophenone with carbon tetrachloride in 1:1 ratio resulted in very heavy carbonisation. The co-pyrolysis of vinyl benzoate with 5% carbon tetrachloride also gave rather heavy carbon deposits. While no explanation is offered for these effects, it does appear as if particularly heavy carbonisation can be induced in these pyrolytic reactions by the presence of a halogen.

5.1.8. Reaction mechanisms.

In the light of the foregoing evidence, it must be concluded that the decomposition of vinyl benzoate occurs by a series of molecular processes, although free radicals may possibly play some part in the decarboxylation reaction.

With regard to the major route R/C^1, it now seems likely that the decomposition proceeds *via* the intermediate benzoylacetaldehyde, the four-membered cyclic transition state suggested by Young's[37] work offering a plausible mechanism, in view of the absence of free-radical chain processes. The failure to detect benzoylacetaldehyde in any pyrolysis of vinyl benzoate is perhaps a little unexpected, as Allan, Forman, and Ritchie[10] report the recovery of

approximately 15% of the pyrolysand on subjecting the ketoaldehyde to pyrolysis at 500°C. The compound, however, is known to be unstable, and, formed in the course of the vinyl benzoate decomposition, it is possibly in a more labile state than normal. In the course of pyrolysing vinyl acrylate, McKinnon[81] obtained an impure 2:4- dinitrophenylhydrazone which, while outside of the limits of a normally acceptable analysis, seemed to correspond best to acryloylacetaldehyde, the postulated intermediate. The overall experimental evidence, therefore, points to the intramolecular rearrangement as offering the most convincing explanation of the mechanism of this route.

Regarding the two minor routes in the decomposition, the process by which an ester decarboxylates remains to be solved. There is only a very weak indication, suggested by the gas analyses of the inhibited runs, that free-radicals play any appreciable part in the reaction, and at present a molecular mechanism is again to be favoured. In that two chemical bonds require to be ruptured, it is to be expected that more than one step is involved in the breakdown. The very minor alkenyl-oxygen scission to benzoic acid and acetylene is also best explained as a molecular process, proceeding *via* Hurd and Blunk's[11] postulated six-membered

chelate ring (see Section 1.2.1.).

5.1.9. The pyrolysis of ethylidene diacetate.

A secondary result which has emerged during the study of vinyl benzoate is the partial suppression of the ethylidene diacetate decomposition in packed vessels. Coffin[54] has reported this reaction to be homogeneous and of first order, in the temperature range 220-268°C, and it is doubtful, therefore, if the inhibition occurring in the present case can be interpretated in terms of surface termination of a free-radical breakdown, particularly as nitric oxide was found to have no effect either upon the diacetate decomposition itself, or upon the initial rise in the course of the vinyl benzoate pyrolysis. However, the obvious alternative explanation of the reaction rate being altered by diffusion effects is not acceptable in view of the fact that a parallel effect was not observed in the subsequent vinyl benzoate decomposition. It seems more likely, despite the conflicting evidence, that deactivation at the walls is occurring. A more extensive study of the decomposition would be required before the nature of this effect could be detailed.

The much higher final pressures attained in the packed vessel can be attributed to a secondary, heterogeneous decomposition of the reaction products.

5.2. The Pyrolysis of Vinyl Acetate.

The short investigation of the vapour-phase pyrolysis of vinyl acetate indicates that the decomposition is parallel to that of vinyl benzoate in being a homogeneous molecular reaction, although an important dissimilarity lies in the occurrence of an acyl-oxygen scission as a major route.

The small rate differences over a wide temperature range must again be accounted for in terms of a diffusion effect in the reactor. Although in this case the volume of the external glass connections was small compared to the reactor, the effective volume of the reactor, as indicated by the area of carbon deposition, was about two-thirds of the total volume. The rather higher pressures obtained in the presence of nitrogen support this view, i.e. that the effective contact time was not constant over a range of temperatures, but was controlled by the rate of diffusion of the gas molecules from the hot zone.

That the high rates in the presence of nitrogen could be due to a reduced number of wall-termination steps in a free-radical chain process is possible, but is dismissed because of the lack of supporting evidence for such processes taking place in the reaction scheme. Nitric oxide was found to be non-effective as an inhibitor ;

nor was any rate decrease observed in a packed vessel. The rate in a packed vessel was similar to that of the empty vessel, and the reaction, therefore, is predominately homogeneous.

6. CONCLUSIONS.

(i) The vapour-phase pyrolysis of vinyl benzoate is a predominately homogeneous reaction, routes R/C^1 and A^2 being completely homogeneous, and route C^2 being partially heterogeneous.

(ii) Free-radical chain processes play no appreciable part in the reaction scheme, and all three routes are thought to proceed through molecular mechanisms. In particular, no new direct evidence has been found for the existence of the intermediate benzoylacetaldehyde in the major route R/C^1, and it is postulated that, as formed in the course of pyrolysis, the ketoaldehyde is in a highly labile state, and is incapable of free existence under such conditions.

(iii) The pyrolysis of vinyl benzoate is retarded by benzoic acid, and mildly catalysed by iodine. Retardation by the acid is probably due to the preferential formation of the addition compound, ethylidene dibenzoate. Catalysis by iodine occurs through activation by collision, rather than through any distinct chemical reaction.

(iv) The pyrolysis of acetophenone is strongly catalysed by iodine.

(v) The pyrolysis of vinyl acetate is a homogeneous reaction. There is no evidence for the existence of free-radical chains in the degradation.

7. APPENDIX.

7.1. The Separation of Vinyl Benzoate and Ethylidene Diacetate by Vapour-Phase Chromatography.

An analytical gas-liquid chromatography column gave indication that the separation of vinyl benzoate and ethylidene diacetate was an easy one, and it was thought possible, therefore, that a purification of vinyl benzoate might be achieved by a quantitative separation of the ester mixture up to volumes of about 0.5 ml. For this purpose a vapour-phase chromatography unit was constructed. The column consisted of a number of glass U-tubes, of 1 inch internal diameter and 2 feet total length. Any number of these tubes could be linked together by means of ground glass joints, and the length of packed column normally used was about 5 feet. The packing material was "Celite 545" containing 20% "Apiezon" M grease as the stationary phase. A dummy column, was used in conjunction with the separating column and the detection unit was a pair of 4 inch long platinum wire katherometers. The complete unit was immersed in an oil bath, lagged with "Fibreglass" sheeting, which was heated by two immersion heaters of 3 kW. and 0.5 kW., the latter

being linked to a "Sunvic" thermostat. Nitrogen was used as the carrier gas, and was metered on a rotameter flow-gauge.

In use, the system was found to have a number of inherent difficulties. The katherometers were found to be extremely sensitive to mechanical shock, even when apparently securely clamped in position, and there was continual difficulty in getting a steady base-line recorded. (In a later analytical column, thermistor beads were found to be much more satisfactory in this respect, but a loss in sensitivity in the detection unit resulted)[82]. However, it was possible to detect the diacetate and benzoate fractions as they emerged from the column. A more serious difficulty lay in the quantity of liquid handled. Using volumes of about 0.25 ml. or greater, there was a tendency for the separate fractions to "tail", i.e., rather than emerging from the column as sharp bands, the two fractions tended to overlap. One reason for this occurrence was undoubtedly due to the initial charge not being vapourised on the column quickly enough, although a 4-inch length of column at the inlet, packed with glass wool, was maintained at about 180°C by means of wire-wound flash heater. Efforts to accelerate the vapourisation of the

charge by increasing the gas flow led to leakage problems at the ground-glass joints because of the high inlet pressures required for the large-diameter column, even when a vacuum pump was attached to the outlet of the column. Finally it was observed that benzoic acid was condensing at the outlet, and it was apparent, therefore, that degradation of the vinyl benzoate was occurring to an appreciable degree as it passed through the unit, probably this degradation taking place mainly at the flash heaters at the inlet and outlet, as the normal working temperature of the oil-bath was about 130°C.

It was evident, therefore, that a quantitative separation of ethylidene diacetate and vinyl benzoate was a major task, and the project was abandoned. The scaling-up of a vapour-phase unit for the separation of relatively large volumes of liquid presents several problems, which are made the more acute when one or more components is liable to suffer thermal degradation. While such a separation could probably be achieved, much development work would be required.

7.2. The Estimation of Acetophenone.

The method of Iddles and Jackson[83] for the gravimetric estimation of carbonyl compounds by

precipitation of the 2:4-dinitrophenylhydrazone was applied to synthetic mixtures of vinyl benzoate and acetophenone. The method did not give reproducible results because of precipitation of the vinyl benzoate containing acetophenone, from the aqueous reagent. An attempt to overcome this by the addition of ethanol again gave anomalous results, the precipitate partially dissolving in the ethanol. Blank runs indicated that some hydrolysis of the ester to acetaldehyde was occurring.

7.3. Gas Analysis.

The solutions used for the absorption gas analysis were :-

Carbon dioxide :- A 30% aqueous solution of potassium hydroxide.

Acetylene[84] :- An aqueous solution of alkaline potassium iodomercurate, prepared by dissolving 500 gm. potassium iodide, 200 gm. mercuric chloride, and 40 gm. sodium hydroxide in 1000 ml. water.

Unsaturated hydrocarbon :- A solution of bromine in 10% potassium bromide, made up to a deep yellow colour.

Carbon monoxide :- Ammoniacal cuprous chloride, prepared by adding 200 gm. cuprous chloride to 750 ml. of 30% aqueous ammonium chloride solution, then adding 0.88

ammonia solution until the reagent solution becomes clear.

It was found that the potassium iodomercurate reagent attacked the mercury in the absorption pipette rapidly, but the acetylene determination could be carried out conveniently over a layer of bromotrichlormethane, which attacked the mercury very slowly. The ethylene determination was also carried out using the same technique, as this facilitated the use of stronger bromine solution, and ensured a more rapid and complete absorption of the unsaturated gas.

8. BIBLIOGRAPHY.

1. Hurd, "The Pyrolysis of Carbon Compounds", Chemical Catalog Co., New York, 1929.
2. Gilchrist and Ritchie, unpublished observations, Glasgow, 1951.
3. Barton, Head and Williams, J.C.S., 1953, 1715.
4. Muir and Ritchie, unpublished observations on "The pyrolysis of cyclo-hexyl benzoate", Glasgow, 1958.
5. Allan, Jones and Ritchie, J.C.S., 1957, 524.
6. McKinnon and Ritchie, ibid., 1957, 2564.
7. Allan, McGee and Ritchie, ibid., 1957, 4700.
8. Oppenheim and Precht, Ber., 1876, 9, 325.
9. Deutsch and Herman, G.P., 515,307/1927.
10. Allan, Forman and Ritchie, J.C.S., 1955, 2717.
11. Hurd and Blunk, J.A.C.S., 1938, 60, 2419.
12. McColl, J.C.S., 1958, 3398.
13. Houtman, van Steenis and Hertjes, Rec. Trav. Chim., 1946, 65, 781.
14. Ingold, "Structure and Mechanism in Organic Chemistry" G. Bell and Sons., London, 1953.
15. Bailey and King, J.A.C.S., 1955, 77, 75.
16. Bailey, Hewitt and King, ibid., p. 357.
17. Bailey and Rosenberg, ibid., p. 73.
18. Bailey, Rosenberg and Young, ibid., 1954, 76, 2251.

19. Bailey and King, J. Org. Chem., 1956, 21, 858.

20. Royals, ibid., 1958, 23, 1822.

21. Eglinton and Rodger, Chem. and Ind., 1959, 256.

22. Froemsdorf, Collins, Hammond and DePuy, J.A.C.S., 1959, 81, 643.

23. Bailey and Hale, ibid., 1959, 81, 647.

24. Peytral, Bull. Soc. Chim., 1922 (4), 31, 118.

25. Calvin and Lemman, J.A.C.S., 1947, 69, 1232.

26. Adickes, Brunnert and Lücker, J. Prakt. Chem., 1931, 130, 163.

27. Anschütz, Ber., 1885, 18, 1945.

28. Bischoff and von Hedenström, ibid., 1902, 35, 4084.

29. Anschütz, ibid., 1927, 60, 1320.

30. Bennet, Jones and Ritchie, J.C.S., 1956, 2628.

31. Cretcher and Pittenger, J.A.C.S., 1925, 47, 2560.

32. Geuther, Annalen, 1858, 106, 249.

33. Laner and Kilburn, J.A.C.S., 1937, 59, 2586.

34. Wislicenus, Ber., 1905, 38, 546.

35. Dieckmann and Stein, ibid., 1904, 37, 3370.

36. Boese and Young, U.S.P., 2,395,800/1946; B.P., 615,523/1949.

37. Young, Frostick, Sanderson and Hauser, J.A.C.S., 1950, 72, 3635.

38. Pohl, ibid., 1951, 73, 5660.

39. Marshall and Todd, Trans. Far. Soc., 1953, 49, 67.

40. Ienger and Ritchie, J.C.S., 1956, 3536.

41. Ienger, Ph.D. Thesis, Glasgow, 1956.

42. Chitwood, U.S.P., 2,251,983/1941.

43. Claisen and Fischer, Ber., 1887, 20, 2191.

44. Hinshelwood, "The Kinetics of Chemical Change", Clarendon Press, Oxford, 1940.

45. Steacie, "Atomic and Free-Radical Reactions", Reinhold Pub. Corp., New York, 1946.

46. Farkas and Melville, "Experimental Methods in Gas Reactions", McMillan and Co., London, 1939.

47. Makens and Eversole, J.A.C.S., 1939, 61, 3203.

48. Blades, Can. J. Chem., 1954, 32, 366.

49. Anderson and Rowley, J. Phys. Chem., 1943, 47, 454.

50. Rudy and Fugassi, ibid., 1948, 52, 357.

51. Warrick and Fugassi, ibid., p. 1314.

52. Gordon, Price and Trotman-Dickenson, J.C.S., 1957, 2813.

53. Steacie, Proc. Roy. Soc., 1930, A.127, 314.

54. Coffin, Can. J. Res., 1931, 636.

55. Burnett and Wright, Trans. Far. Soc., 1953, 49, 1108.

56. Kistiakowsky, Ruhoff, Smith and Vaughan, J.A.C.S., 1935, 57, 876.

57. Sleigh, J. Soc. Chem. Ind., 1937, 15, 430.

58. Adelman, J. Org. Chem., 1949, 14, 1057.

59. Fisher, McLean and Schnizer, ibid., 1953, 18, 1055.

60. Brown, unpublished observation, Glasgow, 1958.

61. Moser, Helv. Chim. Acta., 1931, 14, 971.

62. Howlett, Trans. Far. Soc., 1952, 48, 25.

63. Reed and Thornley, J.C.S., 1957, 3714.

64. Coope and Bryce, Can. J. Chem., 1954, 32, 768.

65. Stavely and Hinshelwood, Proc. Roy. Soc., 1937, A.159, 192.

66. Smith and Hinshelwood, Proc. Roy. Soc., 1944, A.183, 33.

67. Kale and McColl, J.C.S., 1957, 5020.

68. Bilger and Hibbert, J.A.C.S., 1936, 58, 823.

69. Barton and Howlett, Trans. Far. Soc., 1949, 45, 735.

70. Choppin, Frediani, and Kirby, J.A.C.S., 1939, 61, 3176.

71. Barton and Howlett, J.C.S., 1949, 155.

72. Barton and Onyon, Trans. Far. Soc., 1949, 45, 725.

73. Cullis and Priday, Proc. Roy. Soc., 1954, A.224, 308.

74. Berkman, Morrell and Egloff, "Catalysis", Rheinhold Pub. Corp., New York, 1940, p. 456.

75. Bairstow and Hinshelwood, Proc. Roy. Soc., 1933, A.142, 77.

76. Bairstow and Hinshelwood, J.C.S., 1933, 1147; 1155.

77. Gantz and Walters, J.A.C.S., 1940, 62, 996; 1941, 63, 3412.

78. McNesby, Davis, and Gordon, ibid., 1954, 76, 823.

79. Hinshelwood, Clusius, and Hadman, Proc. Roy. Soc., 1930, A.128, 88.

80. Wright, unpublished observation, Glasgow, 1959.

81. McKinnon, Ph.D. thesis, Glasgow, 1959.

82. Cadzow, A.R.C.S.T. thesis, Glasgow, 1959.

83. Iddles and Jackson, Ind. Eng. Chem. Anal., 1934, 454.

84. Hurd and Spence, J.A.C.S., 1929, 51, 3353.